

**CARBON DIOXIDE APPROPRIATION USING ALKANOLAMINE
BLENDS: VAPOR-LIQUID EQUILIBRIUM MODELLING
APPROACH**

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CARBON DIOXIDE APPROPRIATION USING ALKANOLAMINE BLENDS: VAPOR-LIQUID EQUILIBRIUM MODELLING APPROACH

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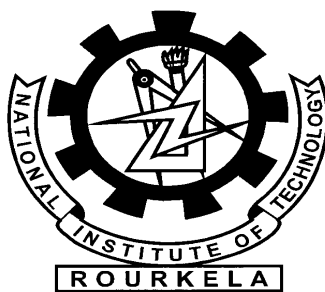
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Supervisor's Certificate

This is to certify that the work presented in this dissertation entitled “Carbon dioxide appropriation using alkanolamine blends: vapor-liquid equilibrium modelling approach” by “*Vaibhav V. Kulkarni*” Roll Number **214CH1100** is a record of original research carried out by him under my supervision and guidance in partial fulfillment of the requirements of the degree of *Master of Technology* in *Department of Chemical Engineering*. Neither this dissertation nor any part of it has been submitted for any degree or diploma to any institute or university in India or abroad.

.....

Prof. Madhusree Kundu

DECLARATION OF ORIGINALITY

I, Vaibhav V. Kulkarni, roll no. 214CH1100 hereby declare that this dissertation entitled “Carbon dioxide appropriation using alkanolamine blends: vapor-liquid equilibrium modelling approach” represents my original work carried out as a postgraduate student of NIT Rourkela and, to the best of my knowledge, it contains no material previously published or written by another person, nor any material presented for the award of any other degree or diploma of NIT Rourkela or any other institution. Any contribution made to this research by others, with whom I have worked at NIT Rourkela or elsewhere, is explicitly acknowledged in the dissertation. Works of other authors cited in this dissertation have been duly acknowledged under the section "References". I have also submitted my original research records to the scrutiny committee for evaluation of my dissertation.

I am fully aware that in case of any non-compliance detected in future, the Senate of NIT Rourkela may withdraw the degree awarded to me on the basis of the present dissertation.

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एषः शोधनिबन्धः मम प्रिय जननीजनकाय,
पूजनीयशिक्षकेभ्यः, परमेश्वराय च समर्पित ।

ABSTRACT

Design of sour-gas treating processes with alkanolamine solvents requires knowledge of vapor liquid equilibrium (VLE) of the aqueous acid gas – alkanolamine systems. An approximate thermodynamic model is developed to correlate and predict the vapor-liquid equilibrium (VLE) of CO₂ in aqueous N-Ethyl Ethanolamine (EAE) solution in the temperature range (303.1-323.1 K). The values of deprotonation constant (K_4) and carbamate reversion constant (K_5) are determined by using the model derived from the VLE data of the ternary system (CO₂ + EAE+ H₂O). The model predictions are in good agreement with the experimental data of CO₂ solubility in aqueous EAE solution available in the open literature. Similarly modified Kent Eisenberg model is validated for the quaternary (CO₂ + AMP+PZ+ H₂O) system. To consider the phase non-ideality in the (CO₂+AMP+PZ+H₂O) system we assumed the equilibrium constants are a function of temperature, CO₂ partial pressure and amine concentration. The adjustable equilibrium constants K_i' are then estimated. Rigorous thermodynamic model i.e. NRTL model is developed and VLE data of (CO₂ + MDEA+ H₂O) is correlated to find out the interaction parameters. The model predictions are in good agreement with the experimental data of CO₂ solubility in aqueous MDEA solution available in the open literature. Density and viscosity of two novel tertiary alkanolamines including 1-(2-hydroxyethyl) piperidine (1-(2-HE)PP) and 2-diethylaminoethanol (DEAE) in their aqueous blends with Piperazine (PZ) have been measured over a temperature range of (303.1, 308.1, 313.1, 318.1, 323.1) K and total amine mass fraction in all the blends was kept constant at 30 %. The mass % ratios of (PZ)/ (1-(2-HE) PP or DEAE) considered for measurements were 3/27, 6/24, 9/21 and 12/18. Density and viscosity of the ternary mixtures were correlated as functions of temperature and amine composition using thermodynamic framework. Modeling and simulation is done in MATLAB platform.

Keywords: Alkanolamine, CO₂, Kent Eisenberg model, modified Kent Eisenberg model, NRTL model.

TABLE OF CONTENTS

List of Figures	vii
List of Tables	viii
Nomenclature	x
Abstract	v
1. Introduction	1
2. Alkanolamine+CO ₂ chemistry and Literature review	6
3. Approximate thermodynamic modelling	11
4. Rigorous thermodynamic modelling	24
5. Physicochemical properties	34
6. Conclusion and future recommendations	53
References	54

LIST OF FIGURES

3.1	Comparison of Model Predicted and Experimentally Measured CO ₂ Equilibrium Partial Pressure over EAE Aqueous Solution in the Temperature Range 303.1-323.1 K.	22
3.2	Comparison of Model Predicted and Experimentally Measured CO ₂ Equilibrium Partial Pressure over (AMP+PZ) Aqueous Solution in the Temperature Range 303.2-393.2 K.	23
4.2	Comparison of Model Predicted and Experimentally Measured CO ₂ Equilibrium Partial Pressure over MDEA Aqueous Solution in the Temperature Range 303.1-323.1 K.	33
5.1	Density of the ternary (PZ (1) + 1-(2-HE)PP (2) + H ₂ O (3)) system at various amine compositions with varying temperature.	47
5.2	Density of the ternary (PZ (1) + DEAE (2) + H ₂ O (3)) system at various amine compositions with varying temperature.	48
5.3	Comparison between experimental and predicted density for ternary (PZ (1) + 1-(2-HE) PP (2) + H ₂ O (3)) system by parity plot.	49
5.4	Comparison between experimental and predicted density for ternary (PZ (1) + DEAE (2) + H ₂ O (3)) system by parity plot.	50
5.5	Viscosity of the ternary (PZ (1) + 1-(2-HE)PP (2) + H ₂ O (3)) system at various amine compositions with varying temperature.	51
5.6	Viscosity of the ternary (PZ (1) + DEAE (2) + H ₂ O (3)) system at various amine compositions with varying tempera	52

LIST OF TABLES

3.1	Temperature dependence of the equilibrium constants and Henry's constant for (CO ₂ +EAE+H ₂ O) system	14
3.2	Temperature dependence of the equilibrium constants and Henry's constant for (CO ₂ +AMP+PZ+H ₂ O) system	19
3.3	Fitting parameters (equilibrium constants) for (CO ₂ + EAE+ H ₂ O) system by kent eisenberg model.	21
3.4	Fitting parameters (equilibrium constants) for (CO ₂ + AMP+PZ+ H ₂ O) system by modified Kent Eisenberg model	21
4.1	Temperature dependence of the equilibrium constants and Henry's constant for (CO ₂ +MDEA+H ₂ O) system	31
4.2	Interaction parameters (equilibrium constants) for (CO ₂ + MDEA+ H ₂ O) system by NRTL model	32
5.1	Comparison of the density data, ρ (g cm ⁻³) of the aqueous 0.623 (M), 1.006 (M) and 1.490 (M) PZ solution from (303.15 to 323.15) K measured in this work with the literature values.	39
5.2	Comparison of the viscosity, η (m Pa S) data of the aqueous 0.623 (M), 1.006 (M) and 1.490 (M) PZ solution from (303.15 to 323.15) K measured in this work with the literature values.	40
5.3	Density, ρ (g cm ⁻³), for the (PZ (1) + 1-(2-HE)PP (2) + H ₂ O (3)) system from (303.15 to 323.15) K with $w_1 + w_2 = 0.3$	40
5.4	Density, ρ (g cm ⁻³), for the (PZ (1) + DEAE (2) + H ₂ O (3)) system from (303.15 to 323.15) K with $w_1 + w_2 = 0.3$	41

5.5	Redlich-Kister equation fitting coefficients of the excess volumes (V_m^E (mL. mol ⁻¹)) for the (PZ (1) + 1-(2-HE)PP(2) + H ₂ O (3)) system.	41
5.6	Redlich-Kister equation fitting coefficients of the excess volumes (V_m^E (mL. mol ⁻¹)) for the (PZ (1) + DEAE (2) + H ₂ O (3)) system.	42
5.7	Fitting parameters for the density, ρ (g cm ⁻³) of the (PZ (1) + 1-(2-HE)PP (2) + H ₂ O (3)) system by eq. (5.6)	42
5.8	Fitting parameters for the density, ρ (g cm ⁻³) of the (PZ (1) + DEAE (2) + H ₂ O(3)) system by eq. (5.6).	43
5.9	Gonzalez model parameter values for (PZ (1) + 1-(2-HE)PP (2) + H ₂ O (3)) System.	43
5.10	Gonzalez model parameter values for (PZ (1) + DEAE (2) + H ₂ O (3)) system.	44
5.11	Viscosity, η (m Pa S) for the (PZ (1) + 1-(2-HE)PP (2) + H ₂ O (3)) system from (303.15 to 323.15) K with $w_1 + w_2 = 0.3$	44
5.12	Viscosity, η (m Pa S) for the (PZ (1) + DEAE (2) + H ₂ O (3)) system from (303.15 to 323.15) K with $w_1 + w_2 = 0.3$	45
5.13	Fitting parameters for the viscosity, η (m Pa S) of the (PZ (1) + 1-(2-HE)PP (2) + H ₂ O (3)) system by eq. (5.6).	45
5.14	Fitting parameters for the viscosity, η (m Pa S) of the (PZ (1) + DEAE(2) + H ₂ O (3)) system by eq. (5.6).	46

NOMENCLATURE

Symbol	Meaning
C_1-C_5	Constants in equation (3.23 & 3.24) and Table 3.1
G	Total Gibbs free energy
F	Objective function for regression
H_{CO_2}	Henry's constant for CO_2 , kPa
K_i	Thermodynamic chemical equilibrium constant
P	Total pressure, kPa
T	Temperature, K
p^{exp}	experimental partial pressure, kPa
p^{cal}	calculated partial pressure, kPa
P_{CO_2}	partial pressure of carbon dioxide, kPa
w_i	weight fraction of i, grams i / total grams solution
x_i	Mole fraction of component i
V_{jk}^E	Excess molar volume for a binary solvent system
V^E	Excess Molar Volume
V_i^0	Molar volume of pure fluids at the system
V_m	Molar volume of the liquid mixture
M_i	Molar mass of pure component i
ρ_m	Measured liquid density
V	Molar volume of solvent, $m^3/kmol$
η_m	Viscosity of the mixture
X	Equilibrium mole fraction
γ	Activity coefficient of component i
∂	Partial derivative

Abbreviations**Meaning**

AMP	2-Amino-2-methyl-1-propanol
CO ₂	Carbon Dioxide
DEA	Diethanolamine
DEAE	Diethyl Ethanolamine
H ₂ O	Water
H ₂ S	Hydrogen Sulphide
MEA	Monoethanolamine
MDEA	N-Methyl-Diethanolamine
PZ	Piperazine
1-(2-HE)PP	1-(2-Hydroxyethyl Pypiridine)
2-PE	2-Piperidineethanol

CHAPTER I***INTRODUCTION***

Carbon dioxide is a natural, fluctuating part of the Earth's air. It is the most essential anthropogenic greenhouse gas and as a result of its expanding gradual addition in the air, world faces the temperature boost impacts and genuine natural issues. CO₂ concentration in the air has expanded generally due to the anthropogenic exercises like natural gas, coal terminated force plant, steel and aluminum industry and because of transportation that utilizations blazing of coal, natural gas and petroleum oil. The presence of Carbon dioxide (CO₂) and hydrogen sulfide (H₂S) makes the gas a corrosive gas. Thus, the raw natural gas must be treated to reduce impurities to acceptable level before it can be in use.

There are a numbers of ways for CO₂ removal. Varieties of processes and their advancement over the years to treat sour gas with the aim of optimizing capital cost and operating cost, meeting gas specifications, and environmental obligations have enriched the technology of sour gas treating.

The major processes available are grouped as follows (Maddox, 1998):

- Absorption Processes (Chemical and Physical absorption)
- Adsorption Process (Solid Surface)
- Physical Separation (Membrane, Cryogenic Separation)
- Hybrid Solution (Mixed Physical and Chemical Solvent)

Presently absorption is the most efficient natural gas purification and post-combustion CO₂ captur technology. When considering solvents for the chemical absorption process, CO₂ absorption rate, CO₂ solubility, heat of absorption, solvent volatility and stability as well as its environmental safety and price are the essential factors directly related to the cost-

efficiency and environmental impact of the capture process. Different types of solvents traditional and new are described below.

1.1 Types of solvents

Alkanolamines

CO₂ absorption into alkanolamine solutions occurs mainly as a result of the amine group of the alkanolamine molecule. It has been suggested that at very high pH, CO₂ can react with the hydroxyl groups of the molecule; however, this reaction is in general not expected to play a significant role in industrial CO₂ capture processes, as the pH of the systems are usually not high enough.

Alkanolamine can be classified into primary, secondary and tertiary depending on the number of alkyl group(s) attached to the nitrogen atom in the structure of the molecule. Monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), N-Ethyl-Ethanolamine (EAE) and 2-amino-2-methyl-1-propanolamine (AMP) are the examples of these amines. Tertiary alkanolamine have the high absorption capacity compared to primary alkanolamines (more than 1). Also there is no formation of carbamate in absorption process which helps to reduce the waste. 1-(2-Hydroxyethyl Pypiridine) and Diethyl Ethanolamine are the examples of tertiary alkanolamines. Disadvantage of this compound is the low rate of absorption. To enhance the rate of absorption promoters like piperazine is used. Being a cyclic symmetric diamine in a six-membered saturated ring, piperazine can theoretically absorb 2 mole of CO₂ for every mole of amine, and it may favor rapid formation of the carbamates. Piperazine has been identified as an effective promoter by many previous investigators (Lensen,2004; Dash et al.,2011; Cullinane and Rochelle,2006; Bishnoi and Rochelle,2004). It is a diamine and can react with CO₂ to form both single and dicarbamate products. In the present scenario the majority of studies centers on ionic liquids, ammonia, and amino acid salt solutions for CO₂ removal.

Ionic liquids

These are salts consisting of anions and cations, but unlike common salts they are liquids even below 373 K (100 °C). Ionic liquids have the advantage of very low vapor pressures, together with high thermal and chemical stability. In addition, these liquids can be used without added water. With CO₂ absorption in common ionic liquids the CO₂ molecules are stored in the cavities between the ions. Adding functionalized groups, such as free amine groups to the ionic liquids, the CO₂ absorbing ability can be increased. But these are not cost effective.

Aqueous ammonia

This is another possibility for replacing the alkanolamines. Unlike alkanolamines, ammonia is stable against degradation and does not cause corrosion problems. Another advantage is the potential low heat requirements; it has been observed that the heat of absorption in the case of ammonia is lower than with MEA. However, a challenge with ammonia is its high vapor pressure.

Aqueous alkaline salts of amino acids

Usually potassium salts but also lithium and sodium salts, are considered alternatives to the currently used alkanolamines. Amino acids have the same amine functionality as alkanolamines, and alkaline amino acid salt solutions thus behave similar towards CO₂ in flue gas. CO₂ absorption using amino acids is a biomimetic approach to CO₂ captures, due to its similarity to CO₂ binding by proteins such as for example hemoglobin. Compared to the solutions of alkanolamines, amino acid salt solutions are characterized by low vapor pressures and higher stability towards oxidative degradation. In addition, they are expected to be environmentally friendly as amino acids are present in nature.

Though these new solvents have good potential to remove CO₂ with respect to alkanolamines, still there are limitations to use these solvents commercially.

1.2 Vapour-Liquid Equilibrium

For the rational design of the gas treating processes, the equilibrium solubility of acid gases over alkanolamines are essential. The solubility data at very low acid gas loading and very high CO₂ partial pressures are scarcely available. It is essential to correlate the available data with a thermodynamic framework, which can be extrapolated confidently to predict the solubility data of that region

In order to establish a solvent to be used in the absorber, a systematic VLE data generation over a wide range of temperature, CO₂ pressure and various relative amine compositions are mandatory. Though various solvents are in use for CO₂ absorption, but a systematic comparison of their performances remained unevaluated so far. Physicochemical properties are of immense significance as far as the design database of gas treating processes is concerned.

The thermodynamic models can be differentiate as approximate and rigorous models.

- In First model approach no ionic strength dependence was considered and the value of the amine protonation constant and the carbamate reversion constant were treated as adjustable parameters and fitted to functions only of temperature. All other equilibrium constants were used at their infinite dilution value as reported in the literature. Kent & Eisenberg^[18], Lee and Mather^[21] are some of the approximate models which are used to correlate the VLE data. Kent & Eisenberg model is widely used due to its simplicity and good ability to correlate experimental data with reasonable accuracy.
- During the recent years, a new generation of rigorous equilibrium models have been developed which is based on the theory of strong electrolyte solutions. These are those based upon direct extensions of the Debye-Hückel limiting law for weak electrolytes and those arising from a combination of a long range term derived from Debye-Hückel theory with a short range term arising from local composition models originally developed for molecular systems. NRTL, Electrolyte NRTL, UNIQUAC model are some of the examples of rigorous thermodynamic models in which non ideality of the solution is described by activity

coefficients and temperature dependence of the alkanolamine protonation and the carbamate reversion were treated as adjustable parameters.

In addition to vapour-liquid equilibrium, knowledge of the physical properties, for example, density and viscosity of solvents is essential for the process design of gas treating units and the design of gas treatment equipment for processes using these solvents.

1.3 Objectives of the present work

The present dissertation aims for the following objective –

- Correlation and prediction of vapor-liquid equilibrium (CO_2 + aqueous alkanolamine blends) using approximate and rigorous thermodynamic modelling.
- To generate and correlate density and viscosity of the used aqueous alkanolamine blends using thermodynamic framework.

1.4 Thesis Layout

Present dissertation begins with introductory note along with an objective and scopes in chapter 1. Literature review and CO_2 + alkanolamine chemistry are documented in chapter 2. Approximate and rigorous thermodynamic modelling of CO_2 + alkanolamine are presented in chapters 3 and 4 respectively. Chapter 5 reports the density and viscosity data generated for various aqueous alkanolamine blends using different temperatures and relative amine compositions. This chapter also documents various thermodynamic correlations used to correlate the generated physicochemical property data. In an ending note thesis concludes in chapter 6 with future recommendations.

CHAPTER II

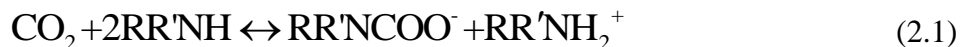
ALKANOLAMINE + CO₂ CHEMISTRY AND LITERATURE REVIEW

Equilibrium thermodynamic here is the combination of physical vapour - liquid equilibrium (VLE) of molecular species and chemical reaction equilibrium that typically occur in aqueous alkanolamine systems. This chapter provides a brief review of the chemical reactions in the CO₂ – alkanolamine systems. A review of previous work on the modeling (approximate and rigorous thermodynamic models) the VLE of CO₂ in single and blended alkanolamines are presented here.

2.1 Alkanoamine - CO₂ reactions

The amine group present in the alkanolamine provides the basicity whereas the hydroxyl group increases the solubility, thus reducing the vapour pressure of aqueous alkanolamine solutions. Following is the reaction scheme for CO₂ + alkanolamine process

2.1.1 Carbamate formation reaction



Where, R' = H for Primary amine, R, R', R'' are alkyl groups for secondary and tertiary amine.

The zwitterion mechanism originally proposed by Caplow (1968) and reintroduced by Danckwerts (1979) is generally accepted as the reaction mechanism for reaction (2.1).



This mechanism comprises two steps: formation of the CO₂-amine zwitterion (reaction (2.2)), followed by base catalyzed deprotonation of this zwitterion (reaction (2.3)). Here B is a base, which could be amine, OH⁻, or H₂O. However, Versteeg and van Swaaij (1988) argued that, for aqueous amine solutions, the contribution of the hydroxyl ion is minor due to its low concentration, and may be neglected without a substantial loss of accuracy. The equilibrium loading capacities of primary and secondary alkanolamines are limited by stoichiometry of reaction (2.1) to 0.5 mole of CO₂/mole of amine. For normal primary and secondary amines e.g. MEA, DEA, EAE etc. the carbamates formed (reaction (2.1)), are quite stable.

2.1.2 Carbamate reversion reaction

If the amine is hindered, the carbamate is unstable and it may undergo carbamate reversion reaction as follows (Sartori and Savage, 1983):



Reaction (2.4) means that for the hindered amines one mole of CO₂ is absorbed per mole of amine. However, a certain amount of carbamate hydrolysis (reaction (2.4)) occurs with all amines so that even with MEA and DEA the CO₂ loading may exceed 0.5, particularly at high pressures and higher contact times (Sartori and Savage, 1983).

2.1.3. CO₂ - tertiary amine reaction

Tertiary amines cannot form carbamates and therefore they act as chemical sink for CO₂ in aqueous solutions simply by providing basicity, the final product being bicarbonate. Hence, the stoichiometry of the CO₂ – tertiary amine reactions is 1 mole of CO₂ per mole of amine.



2.2 Conditions of equilibrium

In a chemical process, equilibrium is the state in which the chemical activities or concentrations of the reactants and products have no net change over time. Usually, this would be the state that results when the forward chemical process proceeds at the same rate as their reverse reaction. The reaction rates of the forward and reverse reactions are generally not zero but, being equal; there are no net changes in any of the reactant or product concentrations. Neglecting surface effects and gravitational, electric and magnetic fields, at thermal and mechanical equilibrium we expect the temperature and pressure to be uniform throughout the entire homogeneous closed system. Gibbs showed that at chemical equilibrium each species must possess a uniform value of chemical potential in all phases between which it can pass. These conditions of phase equilibrium for the closed heterogeneous system can be

$$T^1 = T^2 = \dots T^n$$

$$P^1 = P^2 = \dots P^n$$

$$\mu^1 = \mu^2 = \dots \mu^n$$

Where, $i = 1, 2, 3, \dots, n$, n is the number of phases and m is the number of species present in the closed system.

μ_i is defined by equation

$$\mu_i = \left(\frac{\partial G}{\partial n_{i,T}} \right)_{P, n_{j \neq i}} \quad (2.6)$$

G is the Gibbs free energy of the open system and n_i is the number of moles of component i .

2.3 Chemical equilibria and phase equilibria

In a closed vapour - liquid system containing both electrolytes and non - electrolytes, the electrolyte species will partially or wholly dissociate in the liquid phase to form ionic species. However, unless the system temperature is very high, vapour phase dissociation of electrolyte components will be negligible. Chemical equilibrium governs the distribution of an electrolyte in the liquid phase between its molecular and ionic forms. Since, it is the molecular form of the electrolyte that comes to equilibrium with the same component in the vapour phase, chemical equilibrium significantly affects the phase equilibrium and vice-versa. Both acid gases and alkanolamines may be considered weak electrolytes in solution, thus they dissociate only moderately in a binary aqueous system. The high molar concentrations and high ionic strengths lead to an expected non-ideal behavior of the liquid phase resulting from long range ionic interactions and short range molecular interactions between species in solution.

The temperature dependence of chemical equilibrium constant is often reported as

$$\ln K = C_1 + \frac{C_2}{T} + C_3 \ln T + C_4 T \quad (2.7)$$

2.4 Previous Work

Some of the previous contribution needs to be mentioned as they have been the motivation and starting points behind the present dissertation. Chakravarty *et al.* ^[4] suggested that by blending a tertiary amine (e.g. MDEA) with a primary or secondary amine, the resulting amine mixture may possess both of their advantages such as high loading capacity and enhanced absorption rate. Since then, numerous studies have been conducted on the thermodynamics and kinetics of various amine blends, including MEA/MDEA, DEA/MDEA, MEA/AMP, DEA/AMP, MDEA/AMP. Deshmukh and Mather ^[21] proposed thermodynamic model for the solubility of the acid gases (H₂S and CO₂) in alkanolamine solutions mainly for monoethanolamine. The model is based on the extended Debye-Hückel theory of electrolyte solutions. Tong *et al.* (2013) ^[8] reported new solubility data for carbon dioxide in aqueous blends of 2-amino-2-

methyl-1- propanol (AMP) and piperazine (PZ). Two different solvent blends were studied, both having a total amine mass fraction of 30%:(25 mass % AMP + 5 mass % PZ) and (20 mass% AMP + 10 mass % PZ). Samanta and Bandyopadhyay (2009) ^[22] measured the reaction rate of absorption of CO₂ into PZ activated aqueous AMP solutions using a wetting wall contactor. They found that by replacing 2 mass % AMP with 2 mass % PZ, the reaction rate increased to 3.3 times of the original for 30 mass% AMP; replacing a further 3 mass% of AMP with PZ increased the rate to 4.6 times of the original; and replacing 8 mass% of AMP with PZ increased the rate to 5.6 times the AMP reference value. Alvarez et al., 2006 ^[1] presented the densities and kinematic viscosities of aqueous ternary solutions of 2-(methylamino) ethanol and 2-(ethylamino)-ethanol with diethanolamine, Triethanolamine, N-methyldiethanolamine and 1-amino-1-methyl-1-propanol at temperature range of 298.15-323.15 K. they varied the mass % ratio from 0/50 to 50/0, in 10 mass % steps and total amine concentration was 50 mass %. Samanta and S. Bandyopadhyay, (2006) reported the densities and viscosities of aqueous solutions of piperazine (PZ) and aqueous blends of 2-amino-2-methyl-1-propanol (AMP) and piperazine in the temperature range of (298-323K) for the various mass percentage ratio of piperazine and (AMP). Venkat, G. Kumar and M. Kundu, (2010) ^[20] presented experimental data on the density of aqueous blends of (2-(methylamino)-ethanol (MAE) + 2-amino-2-methyl-1-propanol (AMP)) and (2-(methylamino)-ethanol (MAE) + N-methyl-diethanolamine (MDEA)) in the temperature range of (298.15-323.15K) and within 30% of total amine mass fraction. The experimental values of density and viscosity are correlated with predicted values with good agreement. Paul and Mandal, (2006) ^[23] measured and correlated the density, viscosity for the aqueous blends of 2-piperidineethanol (2-PE) with piperazine (PZ) in the temperature range of (288-333K) and surface surface tension of aqueous blends of PZ with N-methyldiethanolamine, 2-amino-2-methyl-1-propanol, and 2-PE in the temperature range of (293-323K) by keeping total amine mass fraction within 30%.

CHAPTER III

APPROXIMATE THERMODYNAMIC MODELLING

The equilibrium models proposed in this chapter are Kent and Eisenberg and modified Kent and Eisenberg approach for CO₂-alkanolamine-water systems without a serious computational burden and without compromising the accuracy of correlation and prediction capability of the developed model.

3.1 Mathematical model for CO₂+EAE+H₂O System

An approximate thermodynamic model is used for regressing VLE data to estimate the deprotonation and carbamate reversion constants for EAE with appreciable CO₂ loading in aqueous EAE solutions over low to moderately high range of CO₂ pressure.

3.1.1 Chemical Equilibria

The following Chemical Equilibria are involved in aqueous phase for alkanolamine and water system (CO₂+EAE+H₂O)

Ionization of water



Hydration of carbon dioxide



Dissociation of bicarbonate



Dissociation of protonated secondary amine (EAE)



Dissociation of Carbamate



Equilibrium Constants for above reactions are expressed as follows

$$K_1 = [\text{H}^+][\text{OH}^-] \quad (3.6)$$

$$K_2 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} \quad (3.7)$$

$$K_3 = \frac{[\text{H}^+][\text{CO}_3^{--}]}{[\text{HCO}_3^-]} \quad (3.8)$$

$$K_4 = \frac{[\text{H}^+][\text{RR}'\text{R}''\text{N}]}{[\text{RR}'\text{R}''\text{NH}^+]} \quad (3.9)$$

$$K_5 = \frac{[\text{H}^+][\text{RR}'\text{R}''\text{N}]}{[\text{RR}'\text{R}''\text{NCOO}^-]} \quad (3.10)$$

Following balance equations are used in model building

Total amine balance

$$m = [\text{RR}'\text{R}''\text{N}] + [\text{RR}'\text{R}''\text{NH}^+] + [\text{RR}'\text{R}''\text{NCOO}^-] \quad (3.11)$$

Carbon dioxide balance

$$m\alpha = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{--}] + [\text{RR}'\text{R}''\text{NCOO}^-] \quad (3.12)$$

Where α = moles of CO_2 / moles of amine

Electroneutrality

$$[\text{H}^+] + [\text{RR}'\text{R}''\text{NH}^+] = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{--}] + [\text{RR}'\text{R}''\text{NCOO}^-] \quad (3.13)$$

3.1.2 Vapor-Liquid Equilibria

The vapour pressure of CO_2 is related to the free acid gas concentration in the liquid through Henry's law. The vapour-liquid equilibrium of CO_2 over the aqueous alkanolamine solvent, assuming no solvent species in the vapour phase, is given as follows

$$P_{\text{CO}_2} = H_{\text{CO}_2} [\text{CO}_2] \quad (3.14)$$

3.1.3 Thermodynamic Framework

In (CO_2 – EAE – H_2O) system, neutral species; pure alkanolamine (EAE) and H_2O , and ionic species; protonated EAE, HCO_3^- and carbamate ion (EAECOO^-) in the equilibrated liquid phase have been considered. The species like free molecular $[\text{CO}_2]$, $[\text{OH}^-]$ and $[\text{CO}_3^{2-}]$ will have a little effect on the observed equilibria so we can neglect them. We can calculate molar concentrations (solvent) of species in liquid phase based on true molecular or ionic species.

After simplification of equations (3.12) and (3.13) we get,

$$m\alpha = [\text{HCO}_3^-] + [\text{RR}'\text{R}''\text{NCOO}^-] \quad (3.15)$$

$$[\text{RR}'\text{R}''\text{NH}^+] = [\text{HCO}_3^-] + [\text{RR}'\text{R}''\text{NCOO}^-] \quad (3.16)$$

From equation (3.15) and (3.16)

$$m\alpha = [\text{RR}'\text{R}''\text{NH}^+] \quad (3.17)$$

After putting the values of $[\text{RR}'\text{R}''\text{N}]$, $[\text{HCO}_3^-]$, $[\text{RR}'\text{R}''\text{NH}^+]$, from equation (3.11), (3.15) and (3.17) into equation (3.10) and rearranging we get,

$$[\text{RR}'\text{R}''\text{NCOO}^-] = \frac{(K_5 + m) - \left[(K_5 + m)^2 - 4m^2\alpha(1-\alpha) \right]^{\frac{1}{2}}}{2} \quad (3.18)$$

Putting the value of $[\text{RR}'\text{R}''\text{NCOO}^-]$ into equation (3.11) and (3.16) we get,

$$[\text{RR}'\text{R}''\text{N}] = m - m\alpha - Z \quad (3.19)$$

$$[\text{HCO}_3^-] = m\alpha - Z \quad (3.20)$$

$$\text{Where, } Z = \frac{(K_5+m) - \left[(K_5+m)^2 - 4m^2\alpha(1-\alpha) \right]^{1/2}}{2} \quad (3.21)$$

Now the Partial pressure of CO₂ can be expressed as follows by putting the values of [RR'R''NH⁺], [RR'R''NCOO⁻], [RR'R''N] and [CO₂] into equation (3.14) we get,

$$P_{\text{CO}_2} = H_{\text{CO}_2} \frac{K_4 K_5}{K_2} \frac{m\alpha z}{(m-m\alpha-z)^2} \quad (3.22)$$

3.1.4 Equilibrium and henry's constant for CO₂+EAE+H₂O

$$K_i / (\text{kmol m}^{-3}) = \exp \left(C_1 + \frac{C_2}{T} + \frac{C_3}{T^2} + \frac{C_4}{T^3} + \frac{C_5}{T^4} \right) \quad (3.23)$$

$$H_{\text{CO}_2} / ((\text{kPa kmol m}^{-3})^{-1}) = \exp \left(C_1 + \frac{C_2}{T} + \frac{C_3}{T^2} + \frac{C_4}{T^3} + \frac{C_5}{T^4} \right) \quad (3.24)$$

Table 3.1 Temperature dependence of the equilibrium constants and Henry's constant ^[13]
(From Literature) for (CO₂+EAE+H₂O) system

Equilibrium Constant	C ₁	C ₂ ×10 ⁻⁴	C ₃ ×10 ⁻⁸	C ₄ ×10 ⁻¹¹	C ₅ ×10 ⁻¹³
K ₁	39.5554	-9.879	0.568827	-0.146451	0.136145
K ₂	-241.828	29.8253	-1.48528	0.332647	-0.282393
K ₃	-294.74	36.4385	-1.84157	0.415792	-0.354291
H _{CO₂}	20.2629	-1.38306	0.06913	-0.015589	0.01200

Experimental VLE data is taken from literature ^[13] to correlate the data by Kent-Eisenberg model.

3.2 Mathematical model for CO₂+AMP+PZ+H₂O System

3.2.1 Chemical Equilibria

The following Chemical Equilibria are involved in aqueous phase for alkanolamine, piperazine and water system (CO₂+AMP+PZ+H₂O)

Ionization of water



Hydration of carbon dioxide



Dissociation of bicarbonate



Dissociation of protonated secondary amine (AMP)



Reversion of the protonation of PZ



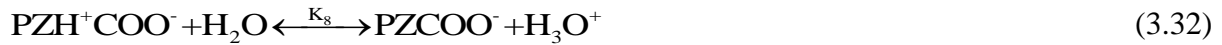
Deformation of first order PZ-carbamate



Deformation of second order PZ-carbamate



Reversion of protonation of the first order PZ-carbamate



Equilibrium Constants for above reactions are expressed as follows

$$K_1 = [\text{H}_3\text{O}^+][\text{OH}^-] \quad (3.33)$$

$$K_2 = \frac{[\text{HCO}_3^-][\text{H}_3\text{O}^+]}{[\text{CO}_2]} \quad (3.34)$$

$$K_3 = \frac{[\text{CO}_3^{--}][\text{H}_3\text{O}^+]}{[\text{HCO}_3^-]} \quad (3.35)$$

$$K_4 = \frac{[\text{R-NH}_2][\text{H}_3\text{O}^+]}{[\text{R-NH}_3^+]} \quad (3.36)$$

$$K_5 = \frac{[\text{PZ}][\text{H}_3\text{O}^+]}{[\text{PZH}^+]} \quad (3.37)$$

$$K_6 = \frac{[\text{PZ}][\text{HCO}_3^-]}{[\text{PZCOO}^-]} \quad (3.38)$$

$$K_7 = \frac{[\text{PZCOO}^-][\text{HCO}_3^-]}{[\text{PZ}(\text{COO}^-)_2]} \quad (3.39)$$

$$K_8 = \frac{[\text{PZCOO}^-][\text{H}_3\text{O}^+]}{[\text{PZCOO}^-\text{H}^+]} \quad (3.40)$$

Following balance equations are used to develop the model

Total amine balance:

$$m_1 = [\text{PZ}(\text{COO}^-)_2] + [\text{PZCOO}^-\text{H}^+] \quad (3.41)$$

$$m_2 = [\text{R-NH}_2] + [\text{R-NH}_3^+] \quad (3.42)$$

Carbon dioxide balance

$$(m_1 + m_2)\alpha = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{--}] + [\text{PZ}(\text{COO}^-)_2] + [\text{PZCOO}^-\text{H}^+] \quad (3.43)$$

Where α = moles of CO_2 / moles of.amine

Electroneutrality

$$[\text{H}_3\text{O}^+] + [\text{R-NH}_3^+] = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{--}] + 2[\text{PZ}(\text{COO}^-)_2] \quad (3.44)$$

3.2.2 Vapor-Liquid Equilibria

The vapour pressure of CO_2 is related to the free acid gas concentration in the liquid through Henry's law. The vapour-liquid equilibrium of CO_2 over the aqueous alkanolamine solvent, assuming no solvent species in the vapour phase, is given as follows

$$P_{\text{CO}_2} = H_{\text{CO}_2} [\text{CO}_2] \quad (3.45)$$

3.2.3 Thermodynamic Framework

In $(\text{CO}_2\text{-AMP-PZ-H}_2\text{O})$ system, neutral species; the most significant species derived from CO_2 are HCO_3^- , $\text{PZ}(\text{COO}^-)_2$, PZCOO^-H^+ . The species like $[\text{CO}_2]$, $[\text{OH}^-]$ and $[\text{CO}_3^{2-}]$ will have a little effect on the observed equilibria so we can neglect them. We can calculate molar concentrations (solvent) of species in liquid phase based on true molecular or ionic species.

After simplification of equations (3.41), (3.42) and (3.43) we get,

$$(m_1 + m_2)\alpha = [\text{HCO}_3^-] + [\text{PZ}(\text{COO}^-)_2] + [\text{PZCOO}^-\text{H}^+] \quad (3.46)$$

$$[\text{HCO}_3^-] = (m_1 + m_2)\alpha - m_1 \quad (3.47)$$

After putting the values of $[\text{R-NH}_3^+]$, $[\text{R-NH}_2]$, $[\text{HCO}_3^-]$, $[\text{PZ}(\text{COO}^-)_2]$ from equation (3.26), (3.34) and (3.36) into equation (3.40) and rearranging we get,

$$[\text{PZCOO}^-\text{H}^+] = Z = \frac{-B + (B^2 - 4AC)^{1/2}}{2A} \quad (3.48)$$

Where,

$$A = \left[2 \left(m_1 + m_2 - \frac{m_1}{\alpha} \right) \alpha - 2B' \right]$$

$$B = \left[\left\{ \left(m_1 + m_2 - \frac{m_1}{\alpha} \right) \left(\frac{m_2 - m_1}{\alpha} - m_1 - m_2 \right) \alpha^2 \right\} + 2B'm_1 + B' \left(\frac{m_1}{\alpha} + m_1 + m_2 \right) \alpha \right]$$

$$C = \left[\left(\frac{m_1}{\alpha} + m_1 + m_2 \right) B'm_1 \alpha \right]$$

$$B' = \frac{K_4 K_7}{K_8}$$

Now the Partial pressure of CO₂ can be expressed as follows by putting the values of and [CO₂],

[R-NH₃⁺], [R-NH₂], [HCO₃⁻] into equation (3.45) we get,

$$P_{CO_2} = \frac{H_{CO_2} K_4 \{(m_1 + m_2) \alpha + m_1 - 2Z\} \{(m_1 + m_2) \alpha - m_1\}}{K_2 [m_2 - \{(m_1 + m_2) \alpha + m_1 - 2Z\}]} \quad (3.49)$$

3.2.4 Phase non-ideality

The treatment of phase non-idealities in the Kent–Eisenberg model was significantly simplified compared to the traditional γ - ϕ approach i.e. the vapour phase non-ideality was neglected while all the non-ideality in the liquid phase was lumped into a number of selected equilibrium constants. In this work K₄, K₇ and K₈ as adjustable equilibrium constants based on the criteria of relative importance. The original form of the Kent–Eisenberg model assumed that the adjustable equilibrium constants were merely functions of temperature. Jou et al. (1982) revised by introducing dependency on loading and amine concentration. Three equilibrium constants were considered to be dependent on temperature, acid gas partial pressure and amine concentration. The final form of the equilibrium constants was as follows.

$$K = \exp \left(a_1 + \frac{a_2}{T} + \frac{a_3}{T^3} + b_1 \alpha_{CO_2} + \frac{b_2}{\alpha_{CO_2}} + \frac{b_2}{\alpha_{CO_2}^2} + b_4 \ln(m) \right) \quad (3.50)$$

To consider the phase non-ideality in the (CO₂+AMP+PZ+H₂O) system we assumed the equilibrium constants are a function of temperature, CO₂ partial pressure and amine concentration. The adjustable equilibrium constants K_i' is used along with the true equilibrium constants to correlate the VLE data and it is expressed as

$$K = \exp \left(a_1 + \frac{a_2(K)}{T} + \frac{a_3(K)}{T} + b_1 \ln(P_{\text{CO}_2}/\text{KPa}) + b_2 (P_{\text{CO}_2}/\text{KPa}) + c_1 m(\text{AMP}) + c_2 m(\text{pz}) \right) \quad (3.51)$$

3.2.5 Equilibrium and henry's constant for CO₂+AMP+PZ+H₂O

$$K_i (\text{H}_2\text{O}/(\text{MPa kg mol}^{-1})) = \exp(a_i (K/T) + b_i \ln(T/K) + c_i (T/K) + d_i) \quad (3.52)$$

Experimental VLE data is taken from literature ^[8] to validate the modified Kent-Eisenberg model.

Table 3.2 Temperature dependence of the equilibrium constants and Henry's constant ^[8] for (CO₂+AMP+PZ+H₂O) system

Equilibrium Constant	a _i	b _i	c _i	d _i
K ₁	-13.445.9	-22.4773	0	140.932
K ₂	-12091.1	-36.7816	0	235.482
K ₃	-12431.7	-35.4819	0	220.067
K ₄	-2546.2	0	0	11.555
K ₅	3814.4	0	-1.5016	14.119
K ₆	3616	0	0	-8.635
K ₇	1322.1	0	0	-3.654
K ₈	-6066.9	-2.29	0.0036	6.822
H _{CO₂}	-9624.4	-28.749	0.01441	192.876

3.3 Method of Solution

The objective function (F) used for optimization is given by

$$F = \sum \left(\frac{P_i^{\text{exp}} - P_i^{\text{cal}}}{P_i^{\text{exp}}} \right)^2 \quad (3.53)$$

This function is optimized by simple minimization of the sum of differences between measured and calculated would weigh the high partial pressure data and almost exclusion of the low partial pressure data.

The MATLAB optimization toolbox has been used extensively for the present work. ‘*fmincon*’ function, which is a constrained optimization function using quasi-Newton and Interior Point algorithm methods, have been used here for minimization of the proposed objective functions with variable bounds.

For the presently formulated phase equilibrium problem the performance of ‘*fmincon*’ proved to be comparatively better than other functions. The converged solutions obtained were initial guess independent.

3.4 Result and Discussion

For (CO₂+ EAE+ H₂O) system values in the table represents the determined equilibrium constants by Kent-Eisenberg model at different temperatures and summarised in table 3.8. Table 3.9 shows the regressed values of adjustable parameters for (CO₂+AMP+ PZ+ H₂O) system. The average absolute percentage deviations between the experimental and model correlated CO₂ pressure is 20% and 13.46% for (CO₂+EAE+H₂O) and (CO₂+AMP+ PZ+ H₂O) system respectively. Figure 3.1 and Figure 3.2 are representative parity plot showing that reasonable agreement between the predicted and experimental VLE data for (CO₂+EAE+H₂O) and (CO₂+AMP+ PZ+ H₂O) system respectively.

Table 3.3 Fitting parameters (equilibrium constants) for (CO₂+ EAE+ H₂O) system by Kent Eisenberg model

Temperature (K)	$K_4/(kmol\ m^{-3})$	$K_5/(kmol\ m^{-3})$
303.1	$1.0880e^{-10}$	1.2144
313.1	$1.2914e^{-10}$	3.7469
323.1	$2.6393e^{-10}$	1.3239

Table 3.4 Fitting parameters (equilibrium constants) for (CO₂+ AMP+PZ+ H₂O) system by modified Kent Eisenberg model

Regressed adjustable parameters	K_4'	K_7'	K_8'
a_1	-0.0363	0.0534	19.6821
a_2	$3.62e^3$	0	0
a_3	$1.47e^{-4}$	0.0291	-1.4732
b_1	1.1748	0	0
b_2	-0.0017	-0.0014	0.017
c_1	-0.0026	0	0
c_2	0	-0.6774	-3.008

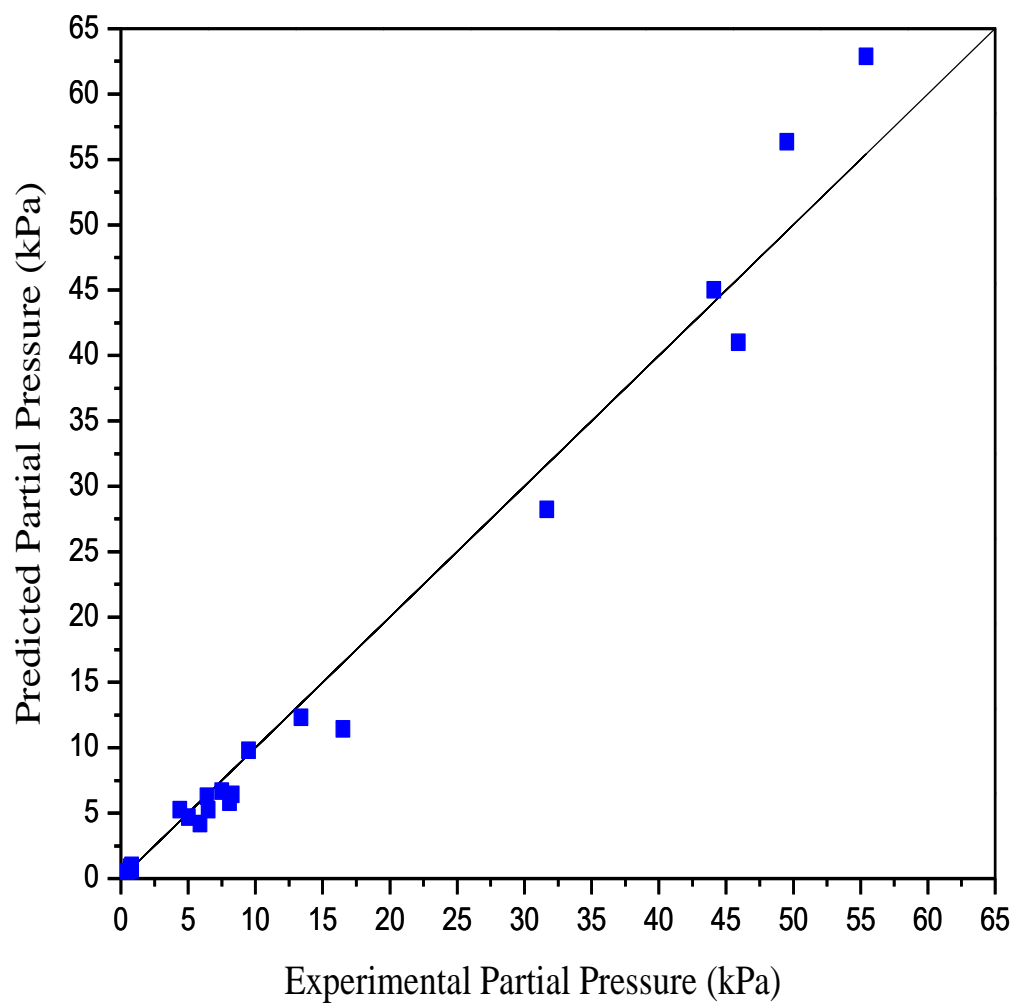


Figure 3.1 Comparison of Model Predicted and Experimentally Measured CO₂ Equilibrium Partial Pressure over EAE Aqueous Solution in the Temperature Range 303.1-323.1 K.

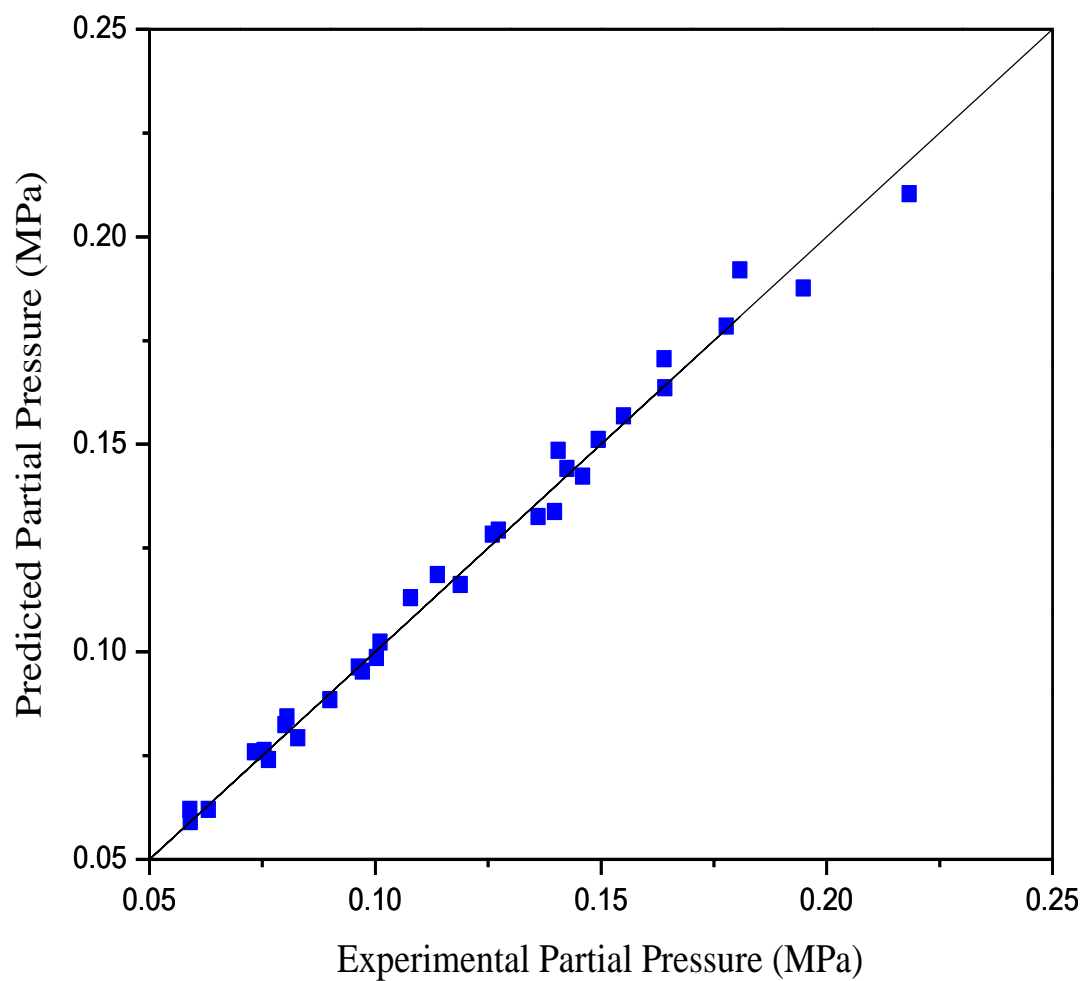


Figure 3.2 Comparison of Model Predicted and Experimentally Measured CO₂ Equilibrium Partial Pressure over (AMP+PZ) Aqueous Solution in the Temperature Range 303.2-393.2 K.

CHAPTER IV**RIGOROUS THERMODYNAMIC MODELLING**

The activity based models provides an insight in to the molecular physics of the system, hence it gives the accurate speciation of the equilibrated liquid phase of the acid gases over alkanolamine solutions. In this chapter, a thermodynamic model based on activity is proposed to correlate and predict the solubility of the acid gas (CO₂) over alkanolamine solutions. Electrolyte NRTL model is used in this chapter to correlate the VLE data.

4.1 Ideal solutions, non-ideal solutions and the activity coefficient

A solution is defined to be ideal if the chemical potential of every species in the solution is a linear function of the logarithm of its mole fraction. That is for every component in an ideal solution the following relation holds:

$$\mu_i = \mu_i^0 + RT \ln x_i \quad (4.1)$$

Where, μ_i^0 is the standard state or reference state chemical potential of component i.

For a real solution, the chemical potential is not a linear function of the logarithm of the mole fraction. In order to preserve the form of equation (4.1) for real solutions, the activity coefficient γ_i is defined such that

$$\mu_i = \mu_i^0 + RT \ln x_i \gamma_i \quad (4.2)$$

Where, γ_i is a function of temperature, pressure, and composition of the solution.

It is emphasized that equation (4.2) should be viewed as a definition of the activity coefficient. μ_i^0 is the chemical potential of component i at the conditions at which γ_i is taken to be unity by convention.

4.2 Standard state convention

The process of identifying reference or standard states at which the activity coefficients of all species in a solution becomes unity is referred to as normalization.

Normalization Convention I

By Normalization Convention 1, the activity coefficient of each component approaches unity as its mole fraction approaches unity at the system temperature and system reference pressure. That is for all components

$$\mu_s = \mu_i^0 + RT \ln x_i \gamma_s \qquad \gamma_s \rightarrow 1 \text{ as } x_s \rightarrow 1 \qquad (4.3)$$

Since this normalization convention holds for all components of a solution, it is known as the symmetric normalization convention; activity coefficients normalized in this manner, are said to be symmetrically normalized. This convention leads to Raoult's law and applied when all components of the solution are liquid at system temperature and pressure.

Normalization Convention II

The reference state for the solvent is different from the reference state for the solutes adopted under Convention II. For the solvent, the reference state is the same as that adopted under Normalization Convention I. The reference state for a solute is taken to be the hypothetical state of pure solute found by extrapolating its chemical potential from infinite dilution in solvent to the pure solute (Denbigh, 1981) at the solution temperature and reference pressure. It is sometimes referred to as the ideal dilute reference state. For a binary solution, Convention II leads to the following expressions for chemical potentials and activity coefficients.

$$\mu_s = \mu_i^0 + RT \ln(x_s \gamma_s) \quad \gamma_s \rightarrow 1 \text{ as } x_s \rightarrow 1 \quad (4.4)$$

$$\mu_s = \mu_i^0 + RT \ln(x_i \gamma_i^*) \quad \gamma_i^* \rightarrow 1 \text{ as } x_i \rightarrow 0 \quad (4.5)$$

Where, the subscripts i and s refer to solute and solvent respectively. Since solute and solvent activity coefficients are not normalized in the same way, Convention II is known as the unsymmetric normalization convention. The superscript, *, on the activity coefficient of the solute is used to indicate that the activity coefficient of this solute approaches unity as its mole fraction approaches zero. This normalization convention leads to Henry's law and is applicable when some components of the solution are gases or solids at the system temperature and pressure.

Normalization Convention III

The concentration of solutes including salts and gases are often measured on molality scale. Accordingly, activity coefficients of these species are also often defined with reference to the molality scale. According to the Normalization Convention III, the activity coefficient of solute and solvent for a binary solution is defined as

$$\mu_s = \mu_i^0 + RT \ln(x_i \gamma_s) \quad \gamma_s \rightarrow 1 \text{ as } x_s \rightarrow 1 \quad (4.6)$$

$$\mu_i = \mu_i^\Delta + RT \ln(m_i \gamma_i^\Delta) \quad \gamma_i^\Delta \rightarrow 1 \text{ as } m_i \rightarrow 0 \quad (4.7)$$

μ_i^0 is the chemical potential of the pure solvent at the system temperature and reference pressure. μ_i^Δ is the chemical potential of the solute in a hypothetical solution of unit molality (Denbigh, 1981). That is, μ_i^Δ is the chemical potential of the solute in a hypothetical ideal solution when m_i and γ_i^Δ are both equal to unity.

4.3 NRTL model

The NRTL (nonrandom, two liquid) equation, was described in detail by Renon (1968), who showed that it appears to be applicable to a wide variety of mixtures for calculating vapor-liquid and liquid-liquid equilibria. For quantitative studies on nonideal properties of liquid mixtures it is convenient to express these properties with excess functions. For liquid mixtures at modest pressures remote from critical conditions, the excess functions are insensitive to pressure; at constant temperature, therefore, the excess functions of such mixtures depend only on liquid composition. The excess Gibbs energy is the excess function of primary interest in chemical engineering and numerous proposals have been made for relating the excess Gibbs energy to liquid composition. The local composition concept provides a convenient method for introducing non-randomness into the liquid-mixture model. Wilson (1964) and Orye and Prausnitz (1965) showed that Wilson's equation is in many respects more useful and more directly applicable to strongly non-ideal mixtures than any other two-parameter equation, and a particular advantage of Wilson's equation for binary systems follows from its straightforward generalization to multicomponent mixtures without need for ternary (or higher) parameters.

Thermodynamic description of vapour-liquid and liquid-liquid equilibria (VLE, LLE) requires knowledge of excess Gibbs energy variation with the liquid phase mixture composition, i.e. one has to know the values of parameters of corresponding GE equations used for calculation of activity coefficients of the mixture components. Already the early attempts to predict multi-component two-phase equilibria showed that the calculation based on binary equilibria only is not able to fit quantitatively the experimental multicomponent equilibrium data.

4.4 Mathematical model for (CO₂+MDEA+H₂O) system

4.4.1 Chemical Equilibria

The following Chemical Equilibria are involved in aqueous phase for alkanolamine and water system (CO₂+MDEA+H₂O)

Ionization of water



Hydration of carbon dioxide



Dissociation of bicarbonate



Dissociation of protonated amine (MDEA)



Equilibrium Constants for above reactions are expressed as follows

$$K_1 = \gamma_{\text{H}^+} [\text{H}^+] \gamma_{\text{OH}^-} [\text{OH}^-] \quad (4.12)$$

$$K_2 = \frac{\gamma_{\text{H}^+} [\text{H}^+] \gamma_{\text{HCO}_3^-} [\text{HCO}_3^-]}{\gamma_{\text{CO}_2} [\text{CO}_2]} \quad (4.13)$$

$$K_3 = \frac{\gamma_{\text{H}^+} [\text{H}^+] \gamma_{\text{CO}_3^{--}} [\text{CO}_3^{--}]}{\gamma_{\text{HCO}_3^-} [\text{HCO}_3^-]} \quad (4.14)$$

$$K_4 = \frac{\gamma_{\text{H}^+} [\text{H}^+] \gamma_{\text{RR}'\text{R}''\text{N}} [\text{RR}'\text{R}''\text{N}]}{\gamma_{\text{RR}'\text{R}''\text{NH}^+} [\text{RR}'\text{R}''\text{NH}^+]} \quad (4.15)$$

Following balance equations are used in model building

Total amine balance:

$$m = [RR'R''N] + [RR'R''NH^+] \quad (4.16)$$

Carbon dioxide balance

$$m\alpha = [CO_2] + [HCO_3^-] + [CO_3^{--}] \quad (4.17)$$

Where α = moles of CO_2 / moles of amine

Electroneutrality

$$[H^+] + [RR'R''NH] = [OH^-] + [HCO_3^-] + 2 [CO_3^{--}] \quad (4.18)$$

4.4.2 Vapor-Liquid Equilibria

The vapour pressure of CO_2 is related to the free acid gas concentration in the liquid through Henry's law. The vapour-liquid equilibrium of CO_2 over the aqueous alkanolamine solvent, assuming no solvent species in the vapour phase, is given as follows

$$PCO_2 = H_{CO_2} [CO_2] \quad (4.19)$$

4.4.3 Thermodynamic Framework

In (CO_2 – MDEA - H_2O) system, neutral species; pure alkanolamine (MDEA) and H_2O , and ionic species; protonated MDEA and HCO_3^- in the equilibrated liquid phase have been considered. The species like free molecular $[CO_2]$, $[OH^-]$ and $[CO_3^{--}]$ will have a little effect on the observed equilibria so we can neglect them. We can calculate molar concentrations (solvent) of species in liquid phase based on true molecular or ionic species. The value of symmetric non-random factor parameter (α) is fixed to 0.2. Interaction parameters are listed in table 4.6.

After simplification of equations (4.12) and (4.13) we get partial pressure as,

$$PCO_2 = HCO_2 \frac{K_4 \gamma_3 \gamma_4 m^2 \alpha^2}{K_2 \gamma_1 (m - m\alpha)} \quad (4.20)$$

Where, $[RR'R''NH^+] = [HCO_3^-] = m\alpha$

The segment contributions from local interactions to the activity coefficients for molecular segments, cationic segments and anionic segments can be calculated from following equations.^[5]

$$\gamma_1 = \exp \left[\left(\frac{X_2 G_{21} \tau_{21} + X_3 G_{31} \tau_{31} + X_4 G_{41} \tau_{41}}{X_2 G_{21} + X_3 G_{31} + X_4 G_{41}} + \frac{X_2 G_{21}}{X_2 G_{21} + X_3 G_{31} + X_4 G_{41}} \left(\tau_{21} - \frac{X_1 G_{21} \tau_{21}}{X_1 G_{21}} \right) + \right. \right. \\ \left. \left. \frac{Y_4 X_3 G_{1343}}{X_2 G_{2343}} \left(\tau_{1343} - \frac{X_2 G_{2343} \tau_{2343}}{X_2 G_{2343}} \right) + \frac{Y_3 X_4 G_{1434}}{X_2 G_{2434}} \left(\tau_{1434} - \frac{X_2 G_{2434} \tau_{2434}}{X_2 G_{2434}} \right) \right] \right]$$

$$\gamma_3 = z_3 \exp \left[\left(Y_4 \frac{X_1 G_{1343} \tau_{1343} + X_2 G_{2343} \tau_{2343}}{X_1 G_{1343} + X_2 G_{2343}} \right) + \frac{X_1 G_{31}}{X_2 G_{21} + X_3 G_{31} + X_4 G_{41}} \left(\tau_{31} - \frac{X_2 G_{21} \tau_{21} + X_3 G_{31} \tau_{31} + X_4 G_{41} \tau_{41}}{X_2 G_{21} + X_3 G_{31} + X_4 G_{41}} \right) \right]$$

$$\gamma_4 = z_4 \exp \left[\left(Y_3 \frac{X_1 G_{1434} \tau_{1434} + X_2 G_{2434} \tau_{2434}}{X_1 G_{1434} + X_2 G_{2434}} \right) + \frac{X_1 G_{41}}{X_2 G_{21} + X_3 G_{31} + X_4 G_{41}} \left(\tau_{41} - \frac{X_2 G_{21} \tau_{21} + X_3 G_{31} \tau_{31} + X_4 G_{41} \tau_{41}}{X_2 G_{21} + X_3 G_{31} + X_4 G_{41}} \right) \right]$$

$$G = \exp(-\alpha\tau)$$

Where, subscript 1,2,3,4 refers to the species MDEA, H₂O, MDEAH⁺, HCO₃⁻, X is equilibrium composition, and z is charge number.

4.4.4 Equilibrium and henry's constant for CO₂+MDEA+H₂O

$$K_i (H_2O / (MPa \text{ kg mol}^{-1})) = \exp(a_i (K/T) + b_i \ln(T/K) + c_i (T/K) + d_i) \quad (4.21)$$

Table 4.1 Temperature dependence of the equilibrium constants and Henry's constant ^[15] for (CO₂+MDEA+H₂O) system

Equilibrium	a _i	b _i	c _i	d _i
K ₁	-13445.9	-22.4773	0	140.932
K ₂	-12092.1	-36.7816	0	235.482
K ₃	-12431.7	-35.4819	0	220.067
K ₄	-8483.95	-13.8328	0	87.39717
H _{CO₂}	-6789.04	-11.4519	-0.010454	94.4914

4.5 Result and discussion

The VLE data of the ternary mixtures were correlated using the NRTL model with correlation deviation of 17.66 % for CO₂ – MDEA - H₂O systems with 2 M MDEA solution. This objective function equation (3.52) is optimized to correlate the experimental data. The MATLAB optimization toolbox has been used for the present work. '*fmincon*' function, which is a constrained optimization function using Interior Point algorithm method, have been used here for minimization of the proposed objective functions with variable bounds. Interaction parameters are summarized in table 4.6. Figure 4.2 shows comparison between experimental and model predicted partial pressure values.

Table 4.2 Interaction parameters of NRTL model for (CO₂+MDEA+H₂O) system.

Estimated Interaction Parameters	
Parameter	Value
$\tau_{\text{MDEA-MDEAH}^+}$	-0.7646
$\tau_{\text{MDEA-HCO}_3^-}$	5.2769
$\tau_{\text{MDEA-H}_2\text{O}}$	5.7094
$\tau_{\text{MDEA-HCO}_3^-, \text{MDEAH}^+ \text{-HCO}_3^-}$	6.6386
$\tau_{\text{H}_2\text{O-MDEAH}^+, \text{HCO}_3^- \text{-MDEAH}^+}$	6.9434
$\tau_{\text{H}_2\text{O-HCO}_3^-, \text{MDEAH}^+ \text{-HCO}_3^-}$	8.8767
$\tau_{\text{H}_2\text{O-HCO}_3^-, \text{MDEAH}^+ \text{-HCO}_3^-}$	9.9623
(AAD)% correlation	17.66.%

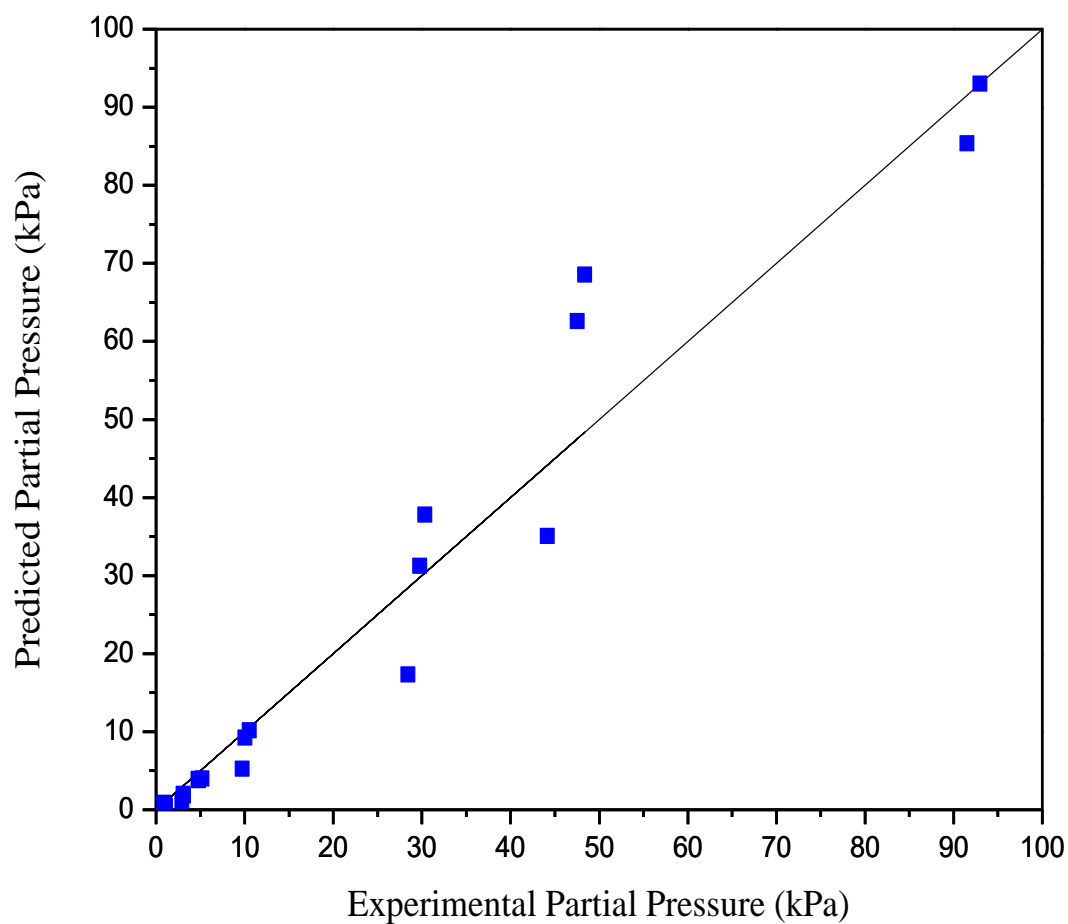


Figure 4.2 Comparison of Model Predicted and Experimentally Measured CO₂ Equilibrium Partial Pressure over 2M MDEA Aqueous Solution in the Temperature Range (303.2-323.2) K.

CHAPTER V**PHYSICOCHEMICAL PROPERTIES**

In this chapter, density and viscosity of aqueous ternary solutions of (1-(2-hydroxyethyl) piperidine + Piperazine) and (2-diethylaminoethanol + Piperazine) at temperature (298.15, 303.15, 308.15, 313.15, 318.15, 323.15) K have been measured for (PZ)/((1-(2-HE) PP), (DEAE)) mass % ratios of 3/27, 6/24, 9/21 and 12/18. Density and viscosity of the solutions is correlated as a function of temperature and amine composition. The total amine composition is fixed to 30%.

5.1 Experimental details**Materials**

2-diethylaminoethanol (DEAE), 1-(2-hydroxyethyl) piperidine (1-(2-HE) PP), and Piperazine (PZ) have been used. The structure of the amines, their purity along their sources are presented in the Table 5.2. Millipore water having conductivity $1 \times 10^{-7} \Omega^{-1} \text{ cm}^{-1}$ and surface tension 72 mN.m^{-1} at 298 K was used for solution preparation. Distilled water degassed by boiling followed by cooling to ambient temperature under vacuum was used for making the alkanolamine solutions. The total amine contents of the solutions were determined by titration with standard HCl using methyl orange indicator.

Density

The densities of aqueous (1-(2-hydroxyethyl) piperidine + Piperazine) and (2-diethylaminoethanol + Piperazine) solutions were measured in the temperature range of (303.15 to 343.15) K using a 25.18 ml Gay-Lussac pycnometer. The pycnometer containing the amine solution was immersed in a constant temperature water bath. The bath temperature was controlled within ± 0.05 K of the desired temperature using a water circulator temperature controller (Polyscience, USA model No: 9712). Once the solution reached the desired temperature, it was weighed to within ± 0.0001 g using an analytical balance (Sartorius, Model: CPA225D). Each reported density value is the average of three measurements. The uncertainty in the measured density was estimated to be $\pm 8.8 \times 10^{-4}$ g.cm⁻³ (combined uncertainty; for coverage factor $k = 2$).

Viscosity

The viscosities of aqueous (1-(2-hydroxyethyl) piperidine + Piperazine) and (2-diethylaminoethanol + Piperazine) solutions were measured using an Ostwald viscometer. The viscometer containing the specific amount of amine solution was immersed in a constant temperature water bath. The bath temperature was controlled within ± 0.05 K of the desired temperature using a water circulator temperature controller (Polyscience, USA model No: 9712). Once the solution reached the desired temperature, time of flow of the solution was recorded. Each reported viscosity data was the average of three measurements with an uncertainty in measurement 0.006 mPa.s at 313 K.

5.2 Results and discussion

Density

The experimental procedure for the density measurement using pycnometer was validated by comparing the generated density data with the data reported by Derks et al.^[27] as presented in Table 5.3. The average absolute deviation in the density measurements for 0.62 mol/L, 1.01

mol/L and 1.49 mol/L PZ solution were found to be 0.024%, 0.023% and 0.022%, respectively. Experimental density data obtained for the system (PZ (1) + 1-(2-HE)PP (2) + H₂O (3)) and (PZ (1) + DEAE (2) + H₂O (3)) are presented in Tables 5.5 and 5.6, respectively, keeping the total amine mass percentage constant as 30. It is revealed in the aforesaid figures that density of the blended solutions decreases as the temperature increases and with decreasing piperazine concentration in the blends.

The excess molar volumes were correlated by using the Redlich-Kister (R-K) equation:

$$V_{jk}^E / ml.mol^{-1} = x_j x_k \sum_{i=0}^n A_i (x_j - x_k)^i \quad (5.1)$$

Where, A_i are pair parameters and are functions of temperature.

$$A_i = a + b(T / K) + c(T / K)^2 \quad (5.2)$$

The excess molar volume of the ternary mixture is presented by equation (5.3) and is calculated by equation (5.4).

$$V^E = V_{12}^E + V_{13}^E + V_{23}^E \quad (5.3)$$

$$V^E = V_m - \sum x_i V_i^0 \quad (5.4)$$

Where, V_m is the molar volume of the liquid mixture (ternary) and V_i^0 is the molar volume of the pure component liquid in the mixture at the system temperature. The molar volume of the liquid mixture from experimentally measured density is calculated by equation (5.5).

$$V_m = \sum \frac{x_i M_i}{\rho_m} \quad (5.5)$$

Where M_i is the molar mass of pure component i , ρ_m is the measured density of the ternary mixture and x_i is the mole fraction of the component i . By equating equation (5.3) and equation (5.4), one can obtain the requisite binary interaction parameters (A_i). A general set of temperature dependent R-K parameters for the ternary system (PZ (1) + 1-(2-HE) PP (2) + H₂O (3)) have been developed using the experimental data with a correlation deviation of 0.032% and are presented in the Table 5.7. Similarly, a set of temperature dependent R-K parameters for (PZ (1) + DEAE (2) + H₂O (3)) ternary system have been developed with a correlation deviation of 0.045% and are presented in the Table 5.8. There is an AAD % of 0.08 and 0.085 between the measured and correlated density for (PZ + 1-(2-HE) PP + H₂O) and (PZ + DEAE + H₂O) systems, respectively.

A Grunberg and Nissan^[20] type model as expressed by equation (5.6) was used to correlate the density data of (PZ + 1-(2-HE)PP + H₂O) and (PZ + DEAE + H₂O) systems with correlation deviations of 0.058% and 0.075% respectively.

$$\rho_m = \sum_{i=1}^n x_i \rho_i + \sum_{i \neq j} A_{ij} x_i x_j \quad (5.6)$$

Where, A_{ij} s' are the binary interaction parameters. ρ_m is the density of the ternary mixture. The temperature dependent Nissan parameters of the two ternary systems are reported in the Tables 5.9 and 5.10. The measured and correlated densities by the R-K equation and equation (5.6) have been compared in the Figures 5.1 and 5.2. The Nissan type equation correlates the generated data more precisely than in comparison to R-K equation.

A semi-empirical model originally proposed by Gonzalez-Olmos and Iglesias^[28] was also used to correlate the generated experimental data, which is expressed by equation (5.7).

$$\rho = \sum_{i=0}^{i=N} (C_i x_1^i + B_i x_2^i) \quad (5.7)$$

$$C_i = \sum_{j=0}^{j=Q} C_{ij} T^j \quad (5.8)$$

$$B_i = \sum_{j=0}^{j=Q} B_{ij} T^j \quad (5.9)$$

Where x_1 is the mole fraction of component 1 and x_2 is the mole fraction of component 2 in the blended solutions. C_{ij} and B_{ij} are polynomial coefficients which are dependent on temperature T as shown by equation (5.8 & 5.9) and are presented in the Tables 5.11 and 5.12 with correlation deviations of 0.075 % and 0.082 % for (PZ + 1-(2-HE) PP + H₂O and (PZ + DEAE + H₂O) systems, respectively. Parity plots among all the measured and model correlated density data are presented in the Figures 5.3, and 5.4 for (PZ + 1-(2-HE) PP + H₂O and (PZ + DEAE + H₂O) systems, respectively.

Viscosity

The experimental procedure for the viscosity measurement using Ostwald viscometer were validated by comparing the experimental viscosity data of aqueous 0.62 mol/L, 1.01 mol/L and 1.49 mol/L PZ solution with the literature value reported by Derks et al.^[27] and are presented in Table 5.4. The average absolute deviation in the density measurements for aqueous 0.62 mol/L, 1.01 mol/L and 1.49 mol/L PZ solution in comparison to the data reported by Derks et al. and were found to be 0.79%, 0.65% and 2.94%, respectively. Experimental viscosity data obtained for the (PZ (1) + 1-(2-HE)PP (2) + H₂O (3)) and (PZ (1) + DEAE (2) + H₂O (3)) systems in the temperature range of (303.15 to 323.15) K are presented in Tables 5.13 and 5.14, respectively, keeping the total amine mass percentage constant at 30 with 'w' as the mass fraction of individual amines present in the solutions.

The viscosities of the ternary mixtures were correlated using the Grunberg and Nissan type^[12] type of expression (equation (5.10)) with correlation deviations of 1.36% and 1.09% , respectively, for (PZ (1) + 1-(2-HE) PP (2) + H₂O (3)) and (PZ (1) + DEAE (2) + H₂O (3)) systems.

$$\ln(\eta_m / mPa.s) = x_1x_2G_{12} + x_2x_3G_{23} + x_1x_3G_{31} \quad (5.10)$$

G_{12} , G_{23} and G_{31} are temperature-dependent pair interaction parameters as expressed by equation (5.11).

$$G_{ij} = a + b(T / K) + c(T / K)^2 \quad (5.11)$$

The temperature dependent fitting parameters for the aforesaid systems are reported in the Tables 5.15 and 5.16, respectively. The measured and correlated viscosities by using the equation (5.10) are presented in the Figures 5.5 and 5.6. It is evident that viscosity of the solution increases as the temperature decreases and piperazine concentration in the blend solution increases.

Table 5.1 Comparison of the density data, ρ (g cm⁻³) of the aqueous 0.623 (M), 1.006 (M) and 1.490 (M) PZ solution from (303.15 to 323.15) K measured in this work with the literature values.

Temperature/K	0.623 (M) aqueous PZ solution		1.006 (M) aqueous PZ solution		1.490 (M) aqueous PZ solution	
	Ref	This work	Ref	This work	Ref	This work
303.15	0.99794	0.99755	0.99979	0.99958	1.00247	1.00243
313.15	0.99425	0.99445	0.99603	0.99573	0.99849	0.99808
323.15	0.98976	0.98989	0.99153	0.99134	0.99386	0.99364
% AAD	0.02%		0.02%		0.02%	

Table 5.2 Comparison of the viscosity, η (m Pa S) data of the aqueous 0.623 (M), 1.006 (M) and 1.490 (M) PZ solution from (303.15 to 323.15) K measured in this work with the literature values.

Temperature/K	0.623 (M) aqueous PZ solution		1.006 (M) aqueous PZ solution		1.490 (M) aqueous PZ solution	
	Ref	This work	Ref	This work	Ref	This work
303.15	0.98	0.987	1.154	1.169	1.402	1.456
313.15	0.787	0.789	0.922	0.916	1.091	1.124
323.15	0.65	0.641	0.747	0.747	0.876	0.893
% AAD	0.79%		0.65%		2.94%	

Table 5.3 Density, ρ (g cm⁻³), for the (PZ (1) + 1-(2-HE)PP (2) + H₂O (3)) system from (303.15 to 323.15) K with $w_1 + w_2 = 0.3$

w_1 / w_2	Temperature / k				
	303.15	308.15	313.15	318.15	323.15
3/27	1.00490	1.00217	0.99909	0.99631	0.99297
6/24	1.00676	1.00399	1.00106	0.99815	0.99478
9/21	1.00828	1.00568	1.00273	0.99992	0.99652
12/18	1.00970	1.00728	1.00445	1.00129	0.99805

Table 5.4 Density, ρ (g cm⁻³), for the (PZ (1) + DEAE (2) + H₂O (3)) system from (303.15 to 323.15) K with $w_1 + w_2 = 0.3$

w_1 / w_2	Temperature / K				
	303.15	308.15	313.15	318.15	323.15
3/27	0.98691	0.98363	0.98020	0.97682	0.97380
6/24	0.99109	0.98721	0.98410	0.98084	0.97753
9/21	0.99456	0.99094	0.98791	0.98453	0.98137
12/18	0.99810	0.99475	0.99158	0.98830	0.98506

Table 5.5 Redlich-Kister equation fitting coefficients of the excess volumes (V_m^E (mL.mol⁻¹)) for the (PZ (1) + 1-(2-HE)PP(2) + H₂O (3)) system.

Estimated (PZ (1) + 1-(2-HE)PP(2) + H ₂ O (3))		
Parameter		Value
A ₀	A	0.0880
	B	-0.0820
	C	0.0029
A ₁	A	-0.0915
	B	0.01047
	C	0.0042
A ₂	A	0.0869
	B	-0.0793
	C	0.0020
(AAD)% correlation		0.0317 %

Table 5.6 Redlich-Kister equation fitting coefficients of the excess volumes (V_m^E (mL.mol⁻¹)) for the (PZ (1) + DEAE (2) + H₂O (3)) system.

Estimated (PZ (1) + DEAE(2) + H ₂ O (3)) (R-K) Parameters		
Parameter		Value
A ₀	A	0.0725
	B	-0.2292
	C	0.0053
A ₁	A	-0.0755
	B	-0.1506
	C	0.0088
A ₂	A	0.0750
	B	-0.2064
	C	0.0042
(AAD)% correlation		0.0448%

Table 5.7 Fitting parameters for the density, ρ (g cm⁻³) of the (PZ (1) + 1-(2-HE)PP (2) + H₂O (3)) system by eq. (5.6)

Estimated Nissan (eq.(5.6)) Parameters		
Parameter		Value
A ₁₂	a	7.2799 e ⁻⁵
	b	0.0012
	c	4.6424 e ⁻⁵
A ₁₃	a	1.7827 e ⁻⁴
	b	0.0169
	c	-5.5021 e ⁻⁵
A ₂₃	a	-3.6546 e ⁻⁴
	b	0.0076
	c	-2.4702 e ⁻⁵
(AAD)%		0.0581%

Table 5.8 Fitting parameters for the density, ρ (g cm⁻³) of the (PZ (1) + DEAE (2) + H₂O(3)) system by eq. (5.6).

Estimated Nissan (eq.(5.6)) Parameters		
Parameter		Value
A ₁₂	a	0.0034
	b	0.5375
	c	-0.0017
A ₁₃	a	0.0369
	b	-5.7001e ⁻⁴
	c	1.7045e ⁻⁶
A ₂₃	a	0.0680
	b	6.5711e ⁻⁴
	c	-5.7445e ⁻⁶
(AAD)% correlation		0.0748%

Table 5.9 Gonzalez model parameter values for (PZ (1) + 1-(2-HE)PP (2) + H₂O (3)) System.

Estimated Gonzalez model Parameters		
C ₀₀ = -0.0124	C ₀₁ = 0.0043	C ₀₂ = 3.21e-06
C ₁₀ = 7.95e-04	C ₁₁ = -0.0221	C ₁₂ = -2.84e-04
C ₂₀ = 0.001	C ₂₁ = -0.0021	C ₂₂ = 6.74e-04
B ₀₀ = -0.0124	B ₀₁ = 0.0043	B ₀₂ = 4.62e-06
B ₁₀ = 6.25e-04	B ₁₁ = -0.0206	B ₁₂ = -2.94e-04
B ₂₀ = 0.0012	B ₂₁ = -3.39e-04	B ₂₂ = -0.0014
AAD		0.0754%

Table 5.10 Gonzalez model parameter values for (PZ (1) + DEAE (2) + H₂O (3)) system.

Estimated Gonzalez model Parameters		
$C_{00} = 3.24\text{e-}04$	$C_{01} = 0.0035$	$C_{02} = 5.511\text{e-}06$
$C_{10} = 4.94\text{e-}04$	$C_{11} = 0.0067$	$C_{12} = -2.80\text{e-}04$
$C_{20} = -7.32\text{e-}06$	$C_{21} = 3.01\text{e-}04$	$C_{22} = -2.45\text{e-}05$
$B_{00} = 3.24\text{e-}04$	$B_{01} = 0.0035$	$B_{02} = -3.54\text{e-}06$
$B_{10} = -2.34\text{e-}05$	$B_{11} = -0.0049$	$B_{12} = -3.34\text{e-}04$
$B_{20} = -6.66\text{e-}06$	$B_{21} = -4.46\text{e-}04$	$B_{22} = -8.03\text{e-}06$
AAD		0.0820%

Table 5.11 Viscosity, η (m Pa S) for the (PZ (1) + 1-(2-HE)PP (2) + H₂O (3)) system from (303.15 to 323.15) K with $w_1 + w_2 = 0.3$

w_1 / w_2	Temperature / K				
	303.15	308.15	313.15	318.15	323.15
3/27	2.8996	2.5683	2.2487	2.0822	1.8342
6/24	2.9471	2.6199	2.2712	2.1039	1.8738
9/21	3.0200	2.6435	2.3175	2.1459	1.8992
12/18	3.2365	2.8164	2.4665	2.2548	2.0663

Table 5.12 Viscosity, η (m Pa S) for the (PZ (1) + DEAE (2) + H₂O (3)) system from (303.15 to 323.15) K with $w_1 + w_2 = 0.3$

w_1 / w_2	Temperature / K				
	303.15	308.15	313.15	318.15	323.15
3/27	3.2342	2.7835	2.3625	2.0457	1.8408
6/24	3.3367	2.9399	2.5397	2.2628	1.9559
9/21	3.5767	3.1305	2.6665	2.3642	2.0350
12/18	3.6108	3.1717	2.7742	2.4180	2.1776

Table 5.13 Fitting parameters for the viscosity, η (m Pa S) of the (PZ (1) + 1-(2-HE)PP (2) + H₂O (3)) system by eq. (5.6).

Estimated Nissan (eq.(5.6)) Parameters		
Parameter		Value
G ₁₂	a	0.0067
	b	0.7121
	c	-0.0044
G ₁₃	a	0.0629
	b	0.3495
	c	-9.006e ⁻⁴
G ₂₃	a	0.0641
	b	0.5265
	c	-0.0015
(AAD)% correlation		1.36 %

Table 5.14 Fitting parameters for the viscosity, η (m Pa S) of the (PZ (1) + DEAE (2) + H₂O (3)) system by eq. (5.6).

Estimated Nissan (eq.(5.6)) Parameters		
Parameter		Value
G_{12}	a	0.00012
	b	0.0185
	c	0.0015
G_{13}	a	0.0031
	b	0.4762
	c	-0.0014
G_{23}	a	0.0038
	b	0.5534
	c	-0.0016
(AAD)%		1.09 %

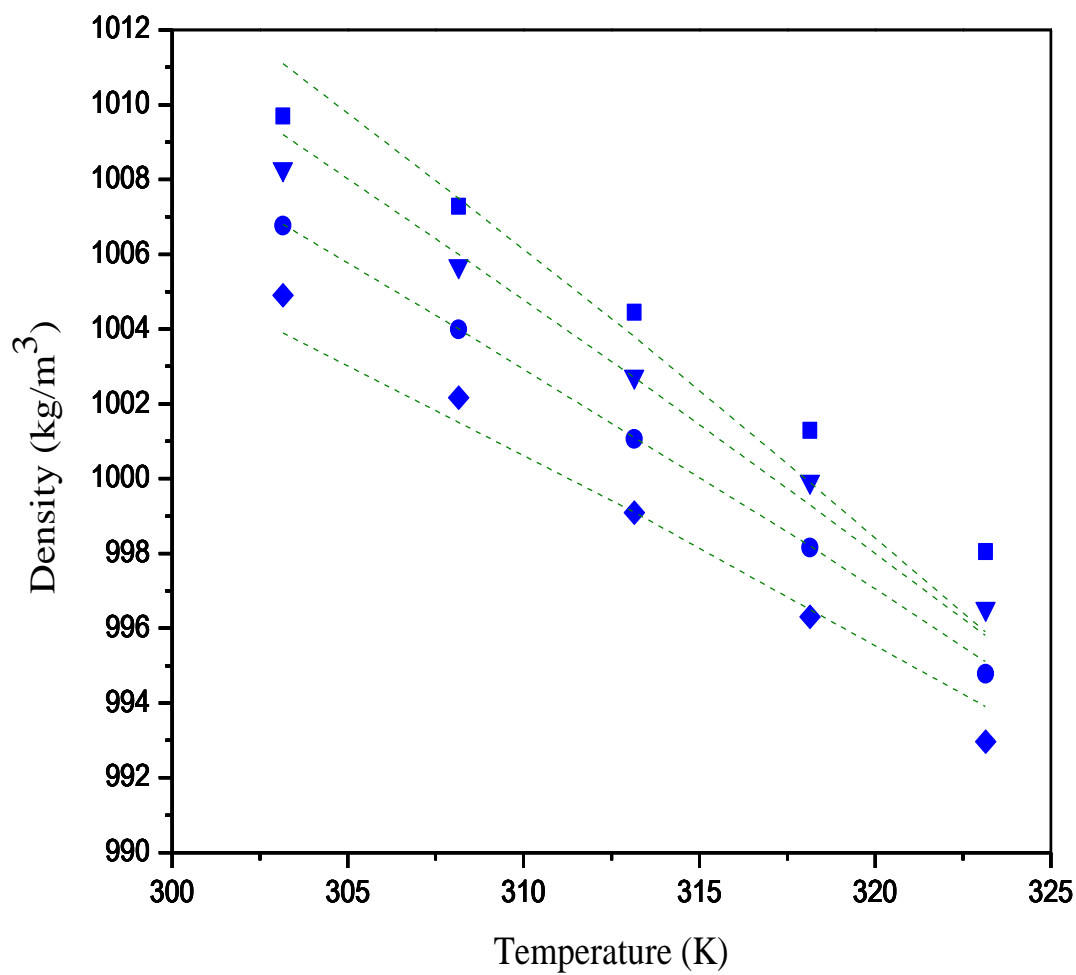


Figure 5.1 Density of the ternary (PZ (1) + 1-(2-HE)PP (2) + H₂O (3)) system at various amine compositions with varying temperature: ♦, (w_1/w_2) = 3/27; ●, (w_1/w_2) = 6/24; ▼, (w_1/w_2) = 9/21; ■, (w_1/w_2) = 12/18. Dotted lines are obtained by R-K equation.

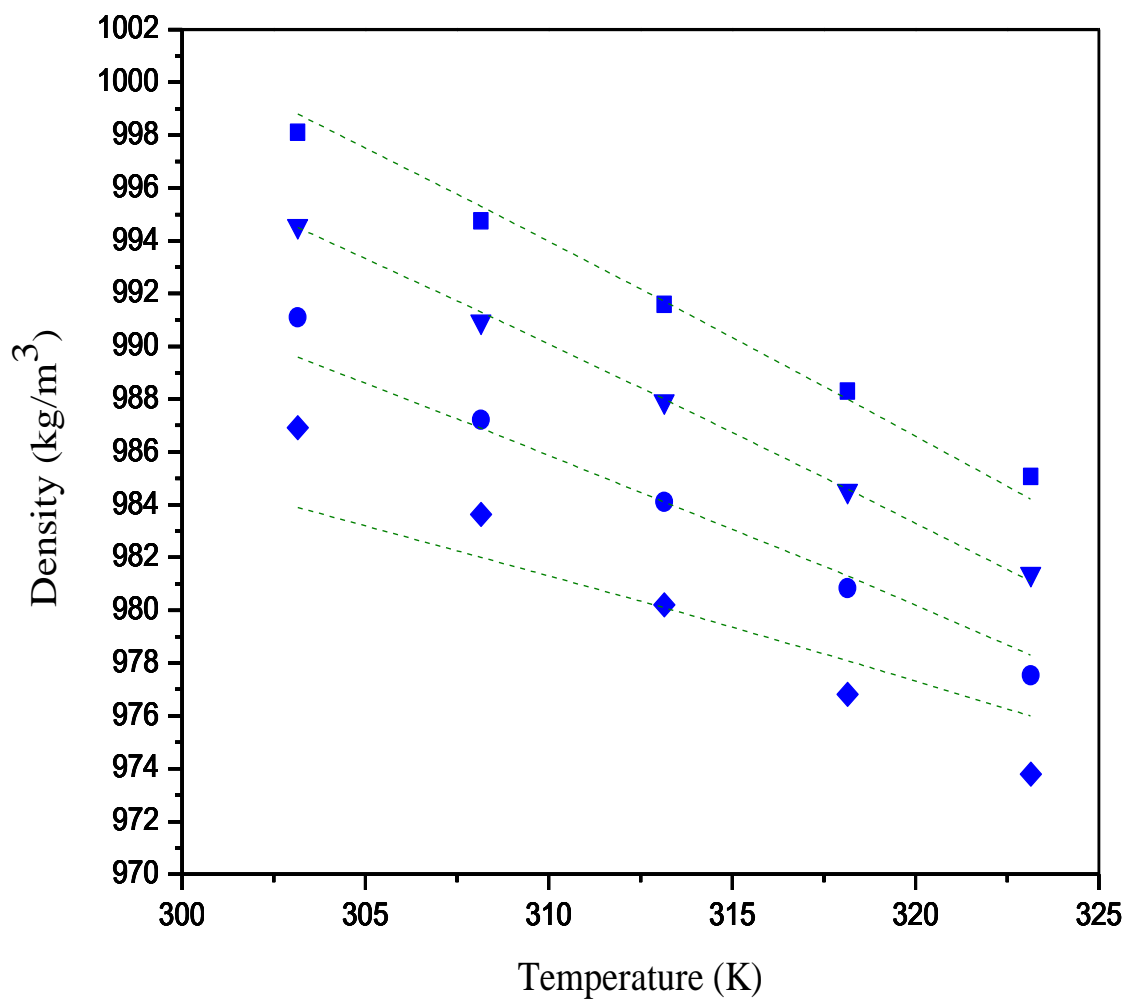


Figure 5.2 Density of the ternary (PZ (1) + DEAE (2) + H₂O (3)) system at various amine compositions with varying temperature: ♦, (w_1/w_2) = 3/27; ●, (w_1/w_2) = 6/24; ▼, (w_1/w_2) = 9/21; ■, (w_1/w_2) = 12/18. Dotted lines are obtained by R-K equation

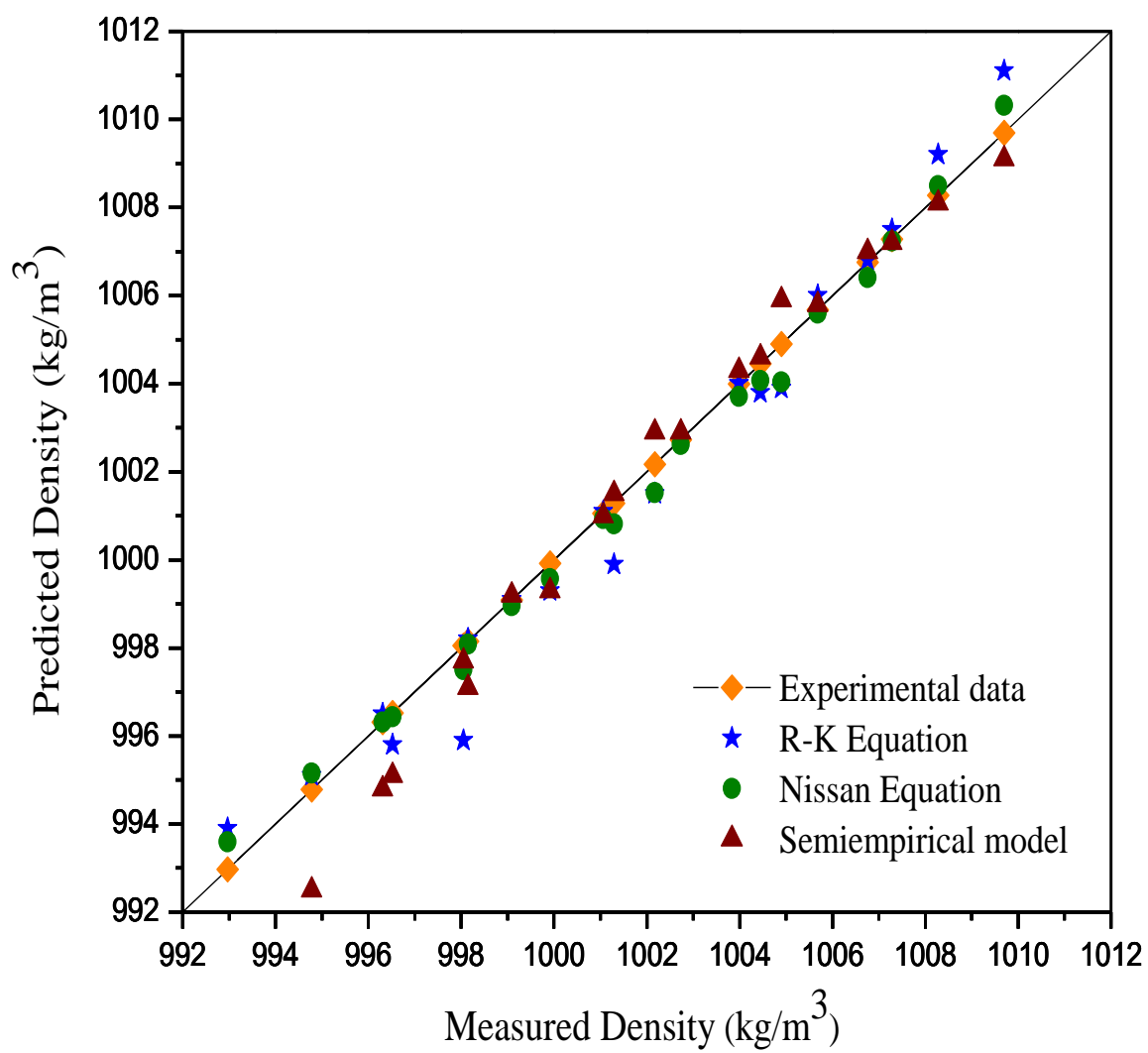


Figure 5.3 Comparison between experimental and predicted density for ternary (PZ (1) + 1-(2-HE) PP (2) + H₂O (3)) system by parity plot.

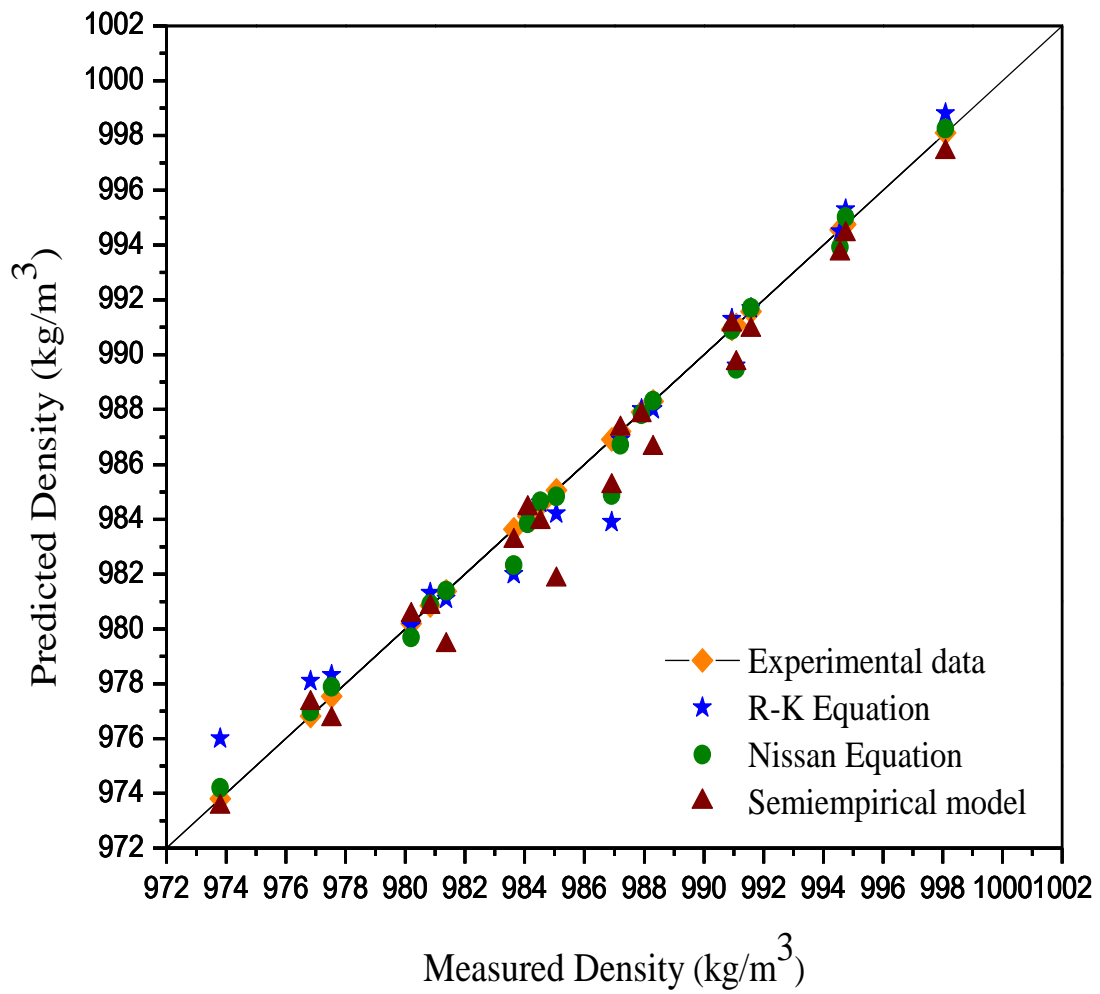


Figure 5.4 Comparison between experimental and predicted density for ternary (PZ (1) + DEAE (2) + H₂O (3)) system by parity plot.

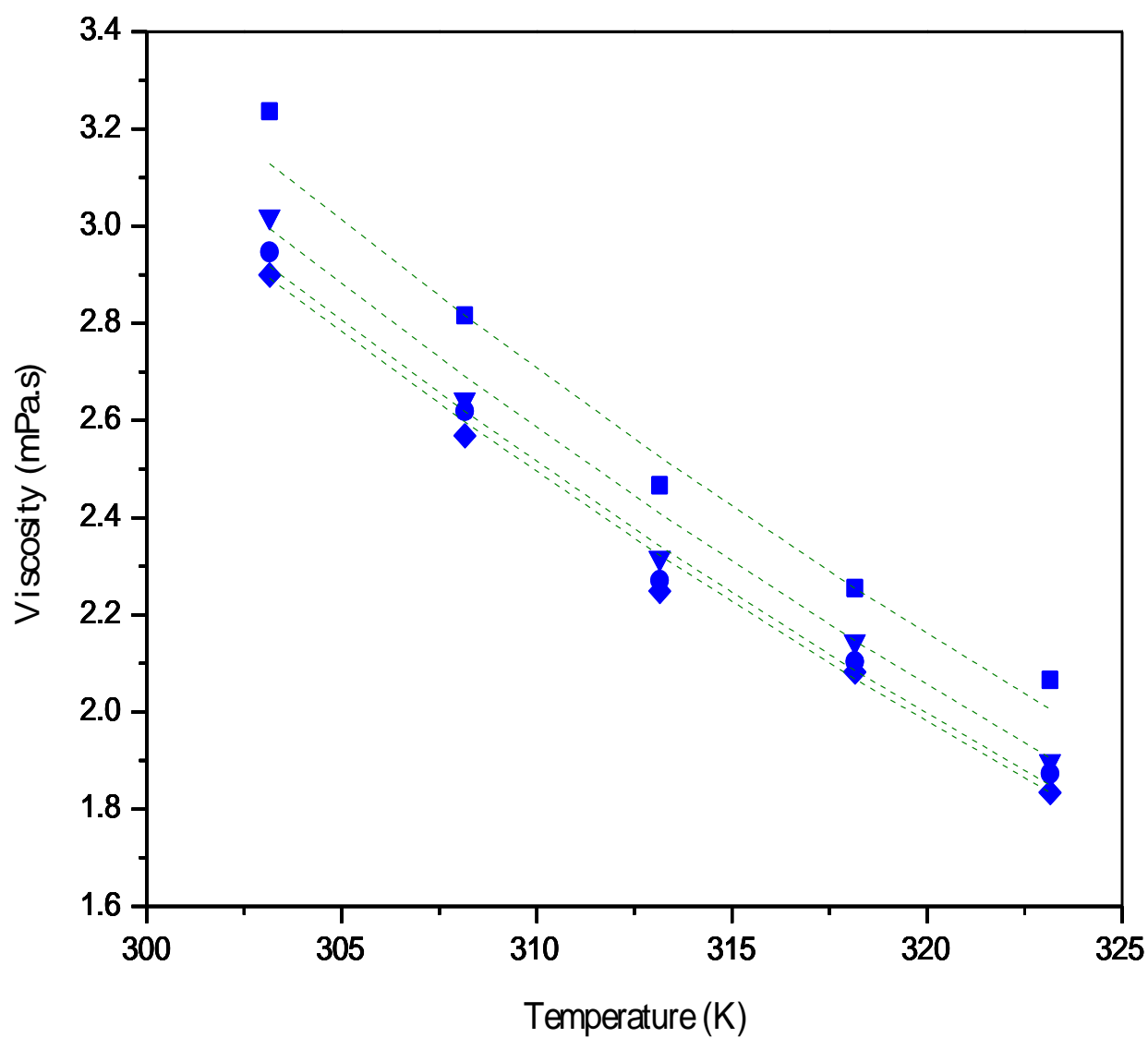


Figure 5.5 Viscosity of the ternary (PZ (1) + 1-(2-HE)PP (2) + H₂O (3)) system at various amine compositions with varying temperature: ◆, (w_1/w_2) = 3/27; ●, (w_1/w_2) = 6/24; ▼, (w_1/w_2) = 9/21; ■, (w_1/w_2) = 12/18. Dotted lines are obtained from equation (5.10).

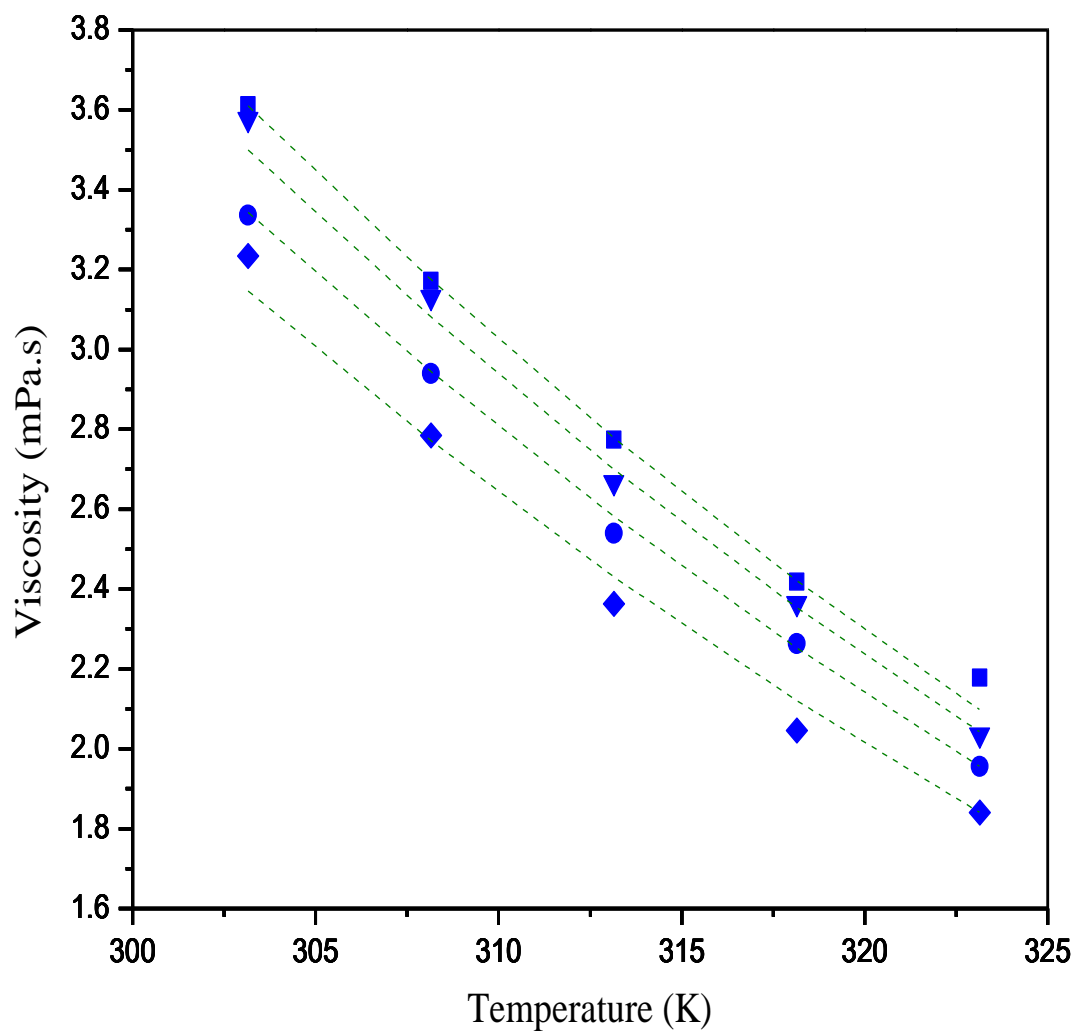


Figure 5.6 Viscosity of the ternary (PZ (1) + DEAE (2) + H₂O (3)) system at various amine compositions with varying temperature: ♦, (w_1/w_2) = 3/27; ●, (w_1/w_2) = 6/24; ▼, (w_1/w_2) = 9/21; ■, (w_1/w_2) = 12/18. Dotted lines are obtained from equation (5.10).

CHAPTER VI**CONCLUSIONS AND FUTURE
RECOMMENDATION**

Conclusions

- Present dissertation has taken into consideration the alkanolamines/blends ($\text{CO}_2 + \text{EAE} + \text{H}_2\text{O}$), ($\text{CO}_2 + \text{AMP} + \text{PZ} + \text{H}_2\text{O}$) system for CO_2 absorption and reveals successful VLE prediction both for ternary and quaternary systems using approximate thermodynamic modelling.
- Present work considers NRTL model to be a significant tool in predicting VLE of the newer alkanolamine blends. In this regard, a generic NRTL model has been developed to predict VLE of ($\text{CO}_2 + \text{MDEA} + \text{H}_2\text{O}$) system.
- In this work density and viscosity data of the newer blends (1-(2-hydroxyethyl) piperidine + Piperazine) and (2-diethylaminoethanol + Piperazine) have been generated and correlated for the wide range of temperatures and amine compositions.

Future recommendation

To predict and correlate the VLE data for (1-(2-hydroxyethyl) piperidine + Piperazine) and (2-diethylaminoethanol + Piperazine) systems for absorption CO_2 modified Kent-Eisenberg and NRTL model.

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